THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

THE THERMAL DEPOLYMERISATION OF POLYSTYRENE.

by

W. W. KERR, B.Sc. (Glas.), A.R.I.C.

SUPERVISOR:
DR. N. GRASSIE.

CHEMISTRY DEPARTMENT,
THE UNIVERSITY,
GLASGOW.

ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346

PREFACE.

This Thesis is submitted for the Degree of Doctor of Philosophy, being an account of original research carried out at The Chemistry Department of The University of Glasgow between September 1953 and June 1957. Due acknowledgment has been made in the text where the results of previous workers in this field have been used, and a list of references to their work has been included at the end of the discussion.

Part of the work, presently to be described, has been published in the Transactions of The Faraday Society and an offprint from that journal is bound in at the end of the type-script.

I would like to take this opportunity of recording my thank to Dr. Norman Grassie not only for the suggestion of the problem and his assistance both in discussion and certain practical aspects of the work, but also for the personal kindness and consideration shown me particularly during a long illness in 1954, which subsequently delayed the submission of this thesis.

I would also like to thank Professor Robertson for the kind interest he has taken in this work and for the provision of laboratory facilities. My thanks are also due to British Celanese Limited for the award of a Celanese Studentship (1953-56), and to The University of Glasgow for the award of the Coats Fellowship (1956-57).

Finally I would like to thank Mr. Alex. Glennie for undertaking many of the molecular weight measurements quoted in the text.

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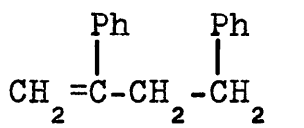
CHAPTER I.

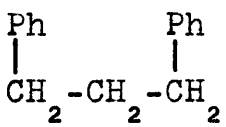
INTRODUCTION

1. Early Experiments and The Random Theory of Degradation.

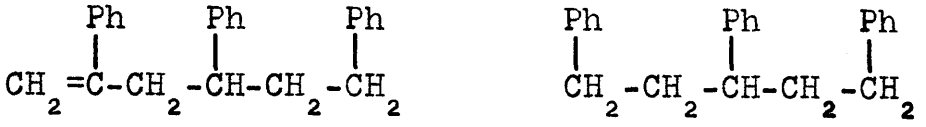
Early studies of the degradation of high polymers were almost entirely confined to naturally occurring compounds. The destructive distillation of natural rubber, towards the end of the last century, and the isolation of dipentene and isoprene from the reaction products played a decisive role in the elucidation of its molecular structure. It was also known about this time that styrene could be recovered from the glassy solid formed by heating it to elevated temperatures. Not until 1935, however, was the degradative distillation of polystyrene critically examined by STAUDINGER and STEINHOFER[1]. From the reaction products they were able to isolate the following compounds in addition to monomeric styrene,



2,4-diphenyl-1-butene.

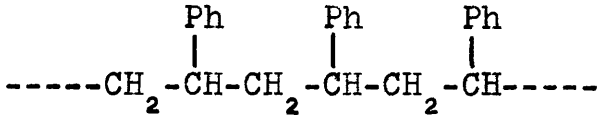


1,3-diphenyl propane.



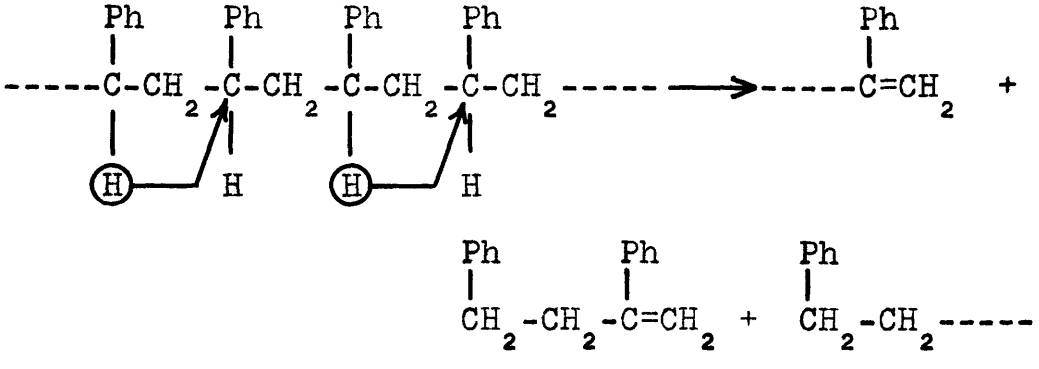
2,4,6-triphenyl-1-hexene. 1,3,5-triphenyl pentane.

and they concluded that polystyrene possesses a head to tail structure:-



MIDGLEY, HENNE and LEICESTER[2] disputed this result but it is now universally accepted.

In the same communication Staudinger suggested that the degradation of polystyrene followed a random pattern[1]. The various products of degradation could be accounted for by a mechanism involving the random breaking of carbon-carbon links along the polymer chain, followed by migration of the tertiary hydrogen atoms:-



In support of this mechanism it was pointed out that the carbon-carbon bond, next but one to an unsaturated centre, is weaker than the normal carbon-carbon linkage[3], a view

which at that time appeared to be supported by the greater thermal stability of polyvinyl cyclohexane[4].

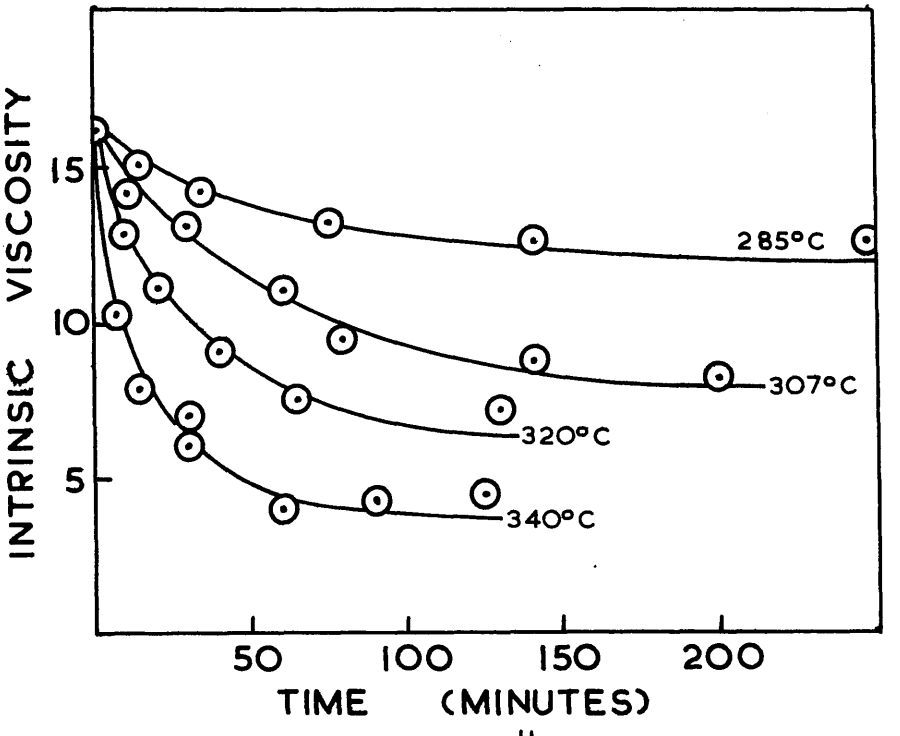
The concept of random degradation in high polymers had been introduced earlier by MEYER, HOPFF and MARK[5], KUHN[6] and FREUDENBERG[7] who applied the theory about 1930 to the hydrolytic degradation of starch and cellulose. The long chain structure of the naturally occurring polysaccharides had by that time been well established, starch and cellulose, for example, being known to consist of glucose residues linked together in chains of varying length. During the hydrolytic degradation of these compounds the viscosity of the system continuously decreases but appreciable amounts of the unit molecule, namely glucose, do not appear early in the reaction. As each act of hydrolysis must proceed independently off all others these results point to a reaction occurring at random along the length of the molecule. KUHN[6], in developing a mathematical treatment for the reaction used a statistical approach in interpreting the random degradation. This, after slight modification to account for the greater reactivity of terminal bonds, was found to satisfy experimental results[8].

It was therefore natural that the production of the unit molecule, or monomer, during the degradation of synthetic polymers should suggest the possibility of

also applying the random theory to these systems. In 1942 VOTINOV, KOBEKO and MAREI[9] examined the degradation of polymethyl methacrylate and polystyrene interpreting their results in terms of Kuhn's random theory. Good agreement between theory and experiment was claimed despite the anomaly of large amounts of monomer produced early in the reaction.

The possibility that free radical played a significant role in these degradation reactions was not clearly established till GRASSIE and MELVILLE[10] re-examined the degradation of polymethyl methacrylate. Basing their results on the changes in molecular weight of the polymer during the reaction and the initial rate of production of monomer they were able to show that degradation is initiated solely at the chain ends and results in the formation of radicals. These then split off monomer in a reverse polymerisation reaction thus explaining the high yields of monomer in the early stages of the reaction. The process is therefore clearly not one of random degradation as would have been apparent to Votinov, Kobeko and Marei had they measured the molecular weights of their polymers during degradation.

About the same time as Grassie and Melville were studying polymethyl methacrylate, JELLINEK studied



JELLINEK[11]

FIG.1.

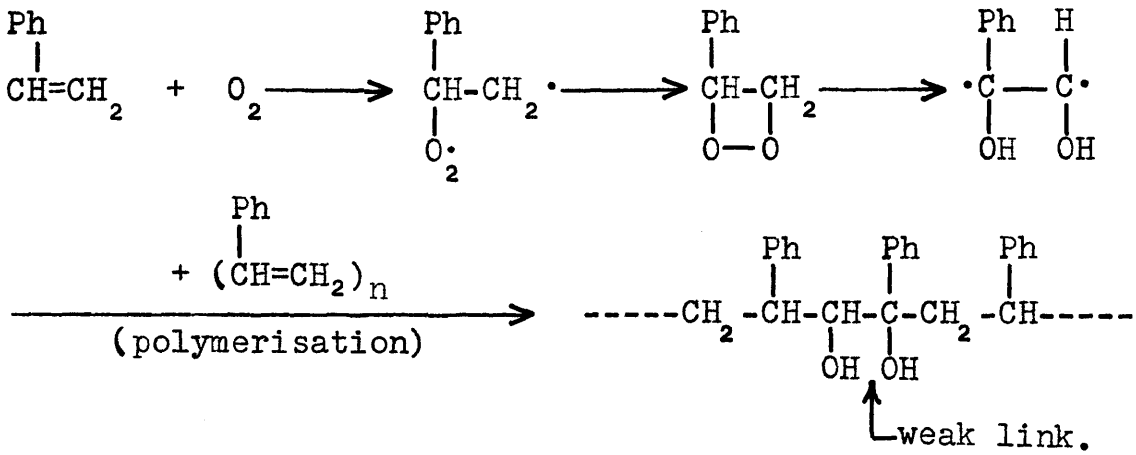
the changes in molecular weight which occurred during the degradation of polystyrene at various temperatures between 240°C and 340°C.[11] He found that the molecular weight of the polymer fell to a limiting value, which appeared to be higher the lower the temperature of degradation. (See Fig.1.) A striking feature of the reaction was the fact that the rapid fall in molecular weight was accompanied by the production of monomer in quantities which were about 10^3 to 10^4 times larger than would be expected on the basis of a random mechanism. Further, the molecular weight data obtained during these experiments was incompatible with a random theory of degradation.

It was therefore becoming apparent that the random theory of degradation was not generally applicable to polymer degradation processes.

2. The Degradation of Polystyrene - The Introduction of The Weak Link Theory.

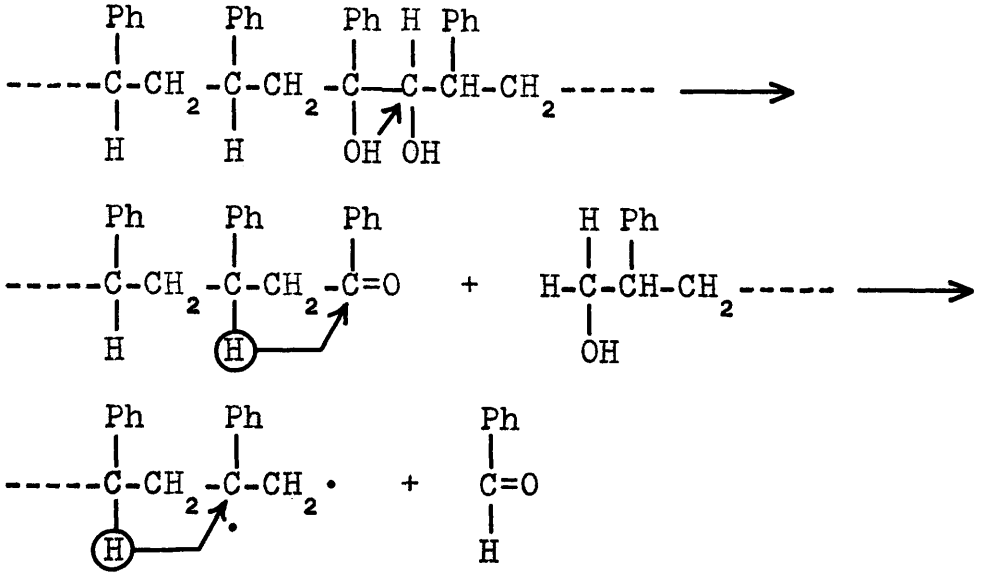
It has been proposed by Jellinek that the experimental results for the degradation of polystyrene are best explained by the existence of a limited number of weak links, which become unstable in the temperature range mentioned above, and which are distributed at random along the polymer chains. These he suggested may

be formed by the incorporation of oxygen into the polymer molecule during polymerisation:-

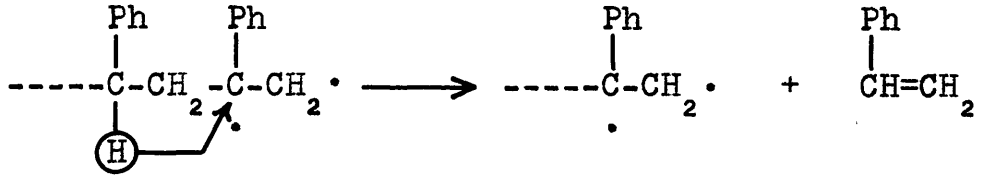


ACHHAMMER[12], examined the infra-red spectra of various undegraded polystyrenes and found no evidence for the presence of hydroxyl groups. It remains doubtful, however, whether the small concentration necessary to account for the large fall in molecular weight could be detected by this method. Jellinek has pointed out that the amount of oxygen required to produce such an effect is of the order of 0.3% by weight and it is interesting to note that amounts of oxygen of this order have been detected in polystyrene samples[13].

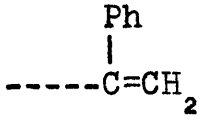
To account for the various features of the reaction Jellinek suggests that degradation is initiated at weak links in the following way -



monomer being produced from the radical chain end -



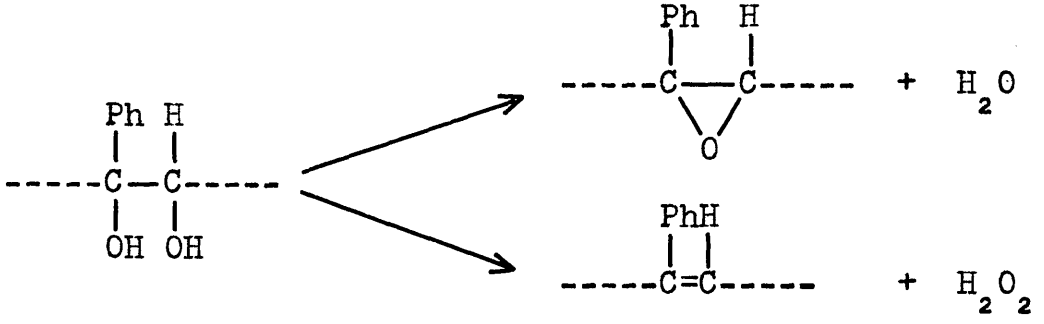
and termination occurring by the formation of a double bond -



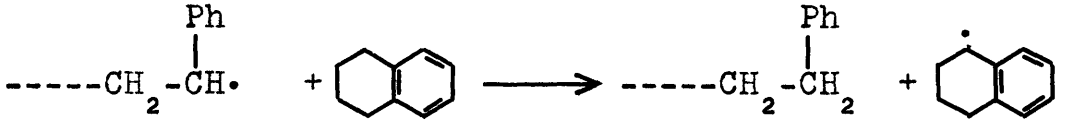
The production of monomer was found to run parallel to the fall in molecular weight and Jellinek was able to deduce that in the course of the weak link scission reaction, during which about 5 to 10% of the polymer degraded, six to ten monomer units were produced per chain end formed.

In order to explain the variation in the fall

in molecular weight with temperature of degradation he assumed that the weak links could disappear without chain scission by one or other of the processes -



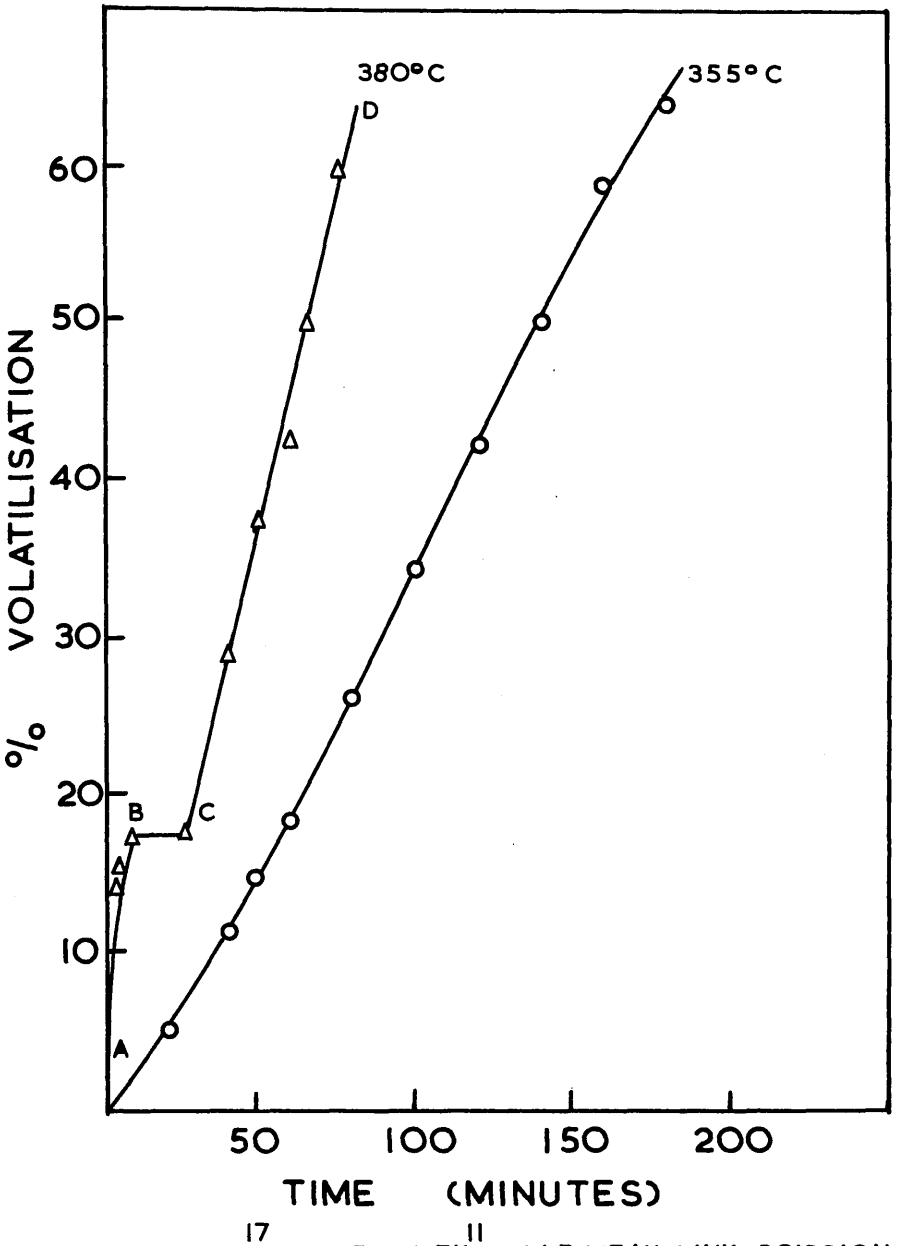
The free radical nature of the reaction was later demonstrated by JELLINEK and SPENCER[14] who carried out degradations in tetralin and naphthalene solutions. The reaction proceeded normally in naphthalene solution but in tetralin no loss in weight of the polymer could be detected. This was attributed to the deactivation of the polymer radicals by transfer to the reactive α-hydrogen atom in the tetralin nucleus -



The weak link theory of degradation, however, has received by no means universal acceptance.

3. The Possible Role of Transfer in The Degradation of Polystyrene.

When the degradation of polystyrene is studied at temperatures above 340°C the predominant reaction is



O MADORSKY[17], Δ JELLINEK[11] (AB-WEAK LINK SCISSION, BC-INHIBITION AND CD-DEPOLYMERISATION)

FIG. 2.

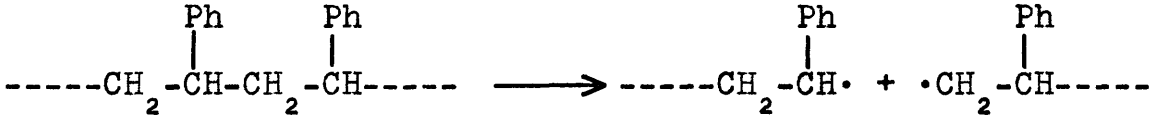
the production of volatile material from the chain ends, the rapid fall in molecular weight associated by Jellinek with weak link scission, being complete early in the reaction. Analysis of the products of degradation reveals the presence of higher chain fragments such as dimer, trimer, tetramer and pentamer as well as monomeric styrene[13,15,16]. This suggests that chain transfer may play a significant role in the reaction.

JELLINEK[11] and MADORSKY[17] both studied the rate of production of volatile material in this temperature range. A typical curve obtained by Jellinek for a polymer of molecular weight 114,000 and by Madorsky for a polymer of molecular weight 106,000 are presented in Fig.2. Jellinek attributes the initial rapid production of volatiles followed by a period of apparent inhibition to the weak link scission phase of the reaction. When this is complete the true depolymerisation reaction follows. Madorsky's curves on the other hand, are smooth from zero to high conversions, and exhibit a rate maximum at about 30 to 40 conversion.

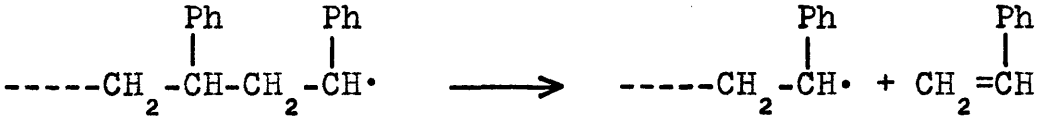
The discontinuity in Jellinek's curves has been the subject of much discussion and considerable doubt has been cast on both the validity and interpretation of these results[18,19,20].

Although Madorsky offers no explanation for the rate maximum in the curves of percentage volatilisation versus time, SIMHA and WALL[21] interpreting the reaction on the basis of a random breaking of bonds followed by intermolecular transfer, have derived a theoretical expression for the rate of conversion to volatile material. The significant feature of this is that it exhibits a rate maximum at 25% conversion. The reaction steps considered are:-

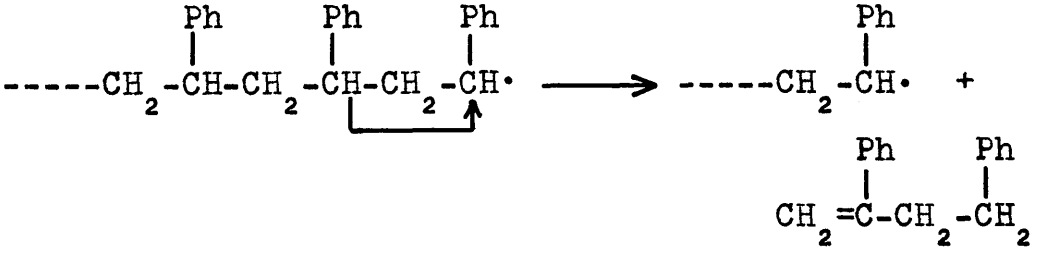
Initiation.



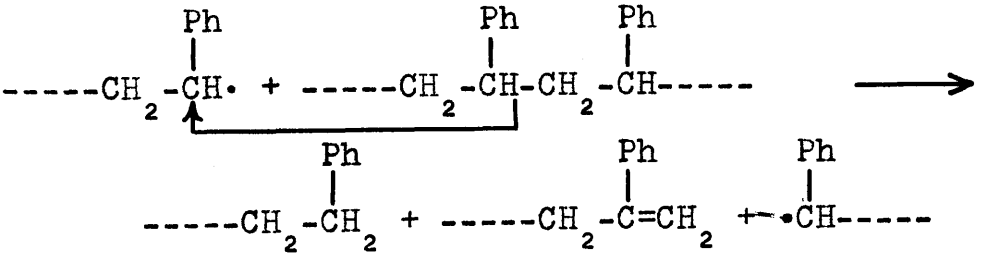
Depropagation.



Intramolecular Transfer.



Intermolecular Transfer.



Termination.

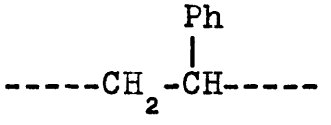
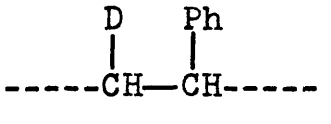
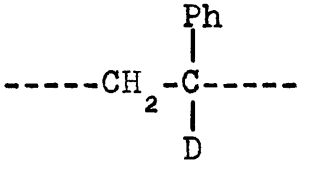
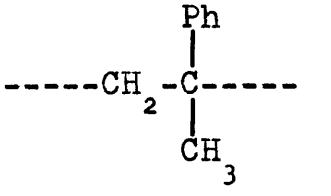
2 Radicals $\longrightarrow$ 2 Polymer Chains.

The difference between the theoretical figure of 25% and the experimental value of 40% is attributed to the fact that the monomer producing and intramolecular transfer reactions are more important than the randomising intermolecular transfer.

TABLE I.

Degradation as a function of molecular structure.

Madorsky and Strauss.[22]

Polymer.	Structure.	Wt. percent of monomer obtained on degradation.
Polystyrene.		42
Poly-β-deutero-styrene.		42
Poly-α-deutero-styrene.		70
Poly-α-methyl-styrene.		100

In a later communication MADORSKY and STRAUSS[22] again draw attention to the importance of chain transfer reactions in the degradation of vinyl polymers. The Percentage of monomer produced during the degradation of several substituted polystyrenes as reported by these authors is quoted in Table I.

Reference to the reaction mechanism of Simha and Wall, quoted above, shows that monomer is produced solely in the propagation step. Higher chain fragments, for example dimer, trimer, tetramer etc., are produced in both the intra- and intermolecular transfer processes. Therefore the yield of monomer obtained during any degradation process will give some measure of the relative importance of the propagation and transfer steps. Thus in poly-α-methylstyrene where the sole product is monomer transfer plays no part in the reaction. Where, however, the methyl group is replaced by hydrogen, as in polystyrene itself, the monomer yield drops to 42% showing that transfer takes place to the tertiary hydrogen atom. This is further confirmed by the results for poly-α-deutero and poly-β-deuterostyrene. The transfer process has been suppressed in poly-α-deuterostyrene as is shown by the increased yield of monomer, but not in poly-β-deuterostyrene.

WALL, HART and BROWN[23] investigated the pyrolysis of poly-α- and poly-β-deuterostyrene, comparing

the rates of degradation of these polymers with the rate of degradation of polystyrene. If the fall in molecular weight was due to weak link scission, as suggested by Jellinek, they assumed no difference in the rates of degradation of polystyrene and poly-α-deuterostyrene should occur, whereas if intermolecular transfer plays a significant role in the reaction the rate of degradation of poly-α-deuterostyrene would be expected to be smaller than that of polystyrene. The rate of degradation of poly-α-deuterostyrene, as reflected by measurements of the intrinsic viscosity of the polymer as it degraded, was found to be of the order of half that of polystyrene. It was therefore suggested that the operative mechanism in the degradation of polystyrene is not weak link scission but intermolecular transfer.

4. Discussion of The Weak Link and Transfer Theories of Degradation.

The reaction scheme required by both these theories is adequately represented by that proposed by Simha and Wall (Page 10). The difference between these theories lies in different modes of initiation and the admission or exclusion of intermolecular transfer.

According to Jellinek initiation takes place exclusively by the breaking of weak links which are

distributed at random along the polymer chain. The production of volatile material occurs through propagation (i.e. reverse polymerisation) and intramolecular transfer. The rapid fall in molecular weight which characterises the reaction is therefore a function of the initiation process alone.

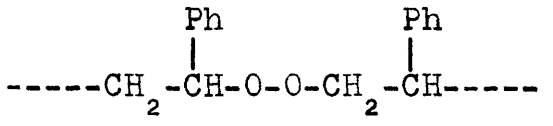
The inclusion of intermolecular transfer in the reaction scheme, as suggested by Simha and Wall, will effectively obscure any decrease in molecular weight occurring as the result of the initiation step, due to the subsequent predominance of randomising transfer. Chain scission at weak links, with the production of radicals, which might then propagate the degradation through intermolecular transfer, would therefore also be accounted for by Simha's mechanism and theory. This type of degradation pattern has been proposed by OAKES and RICHARDS[24] to account for the degradation of polyethylene. It is, however, difficult to explain on the basis of this theory the relatively high limiting value to which the molecular weight falls. A continuous fall to low values would be predicted. In addition the theory does not adequately account for the position of the rate maximum.

Finally the results of Wall, Hart and Brown must be reconsidered. The increased yield of monomer

from poly-α-deuterostyrene together with the lower rate of degradation of this polymer are interpreted as indicating intermolecular transfer as the reaction mechanism. Both results depend on the lower rate of transfer of deuterium. Thus if weak links are present in the molecule and chain scission at these points involves transfer of the tertiary hydrogen atom the slower rate of degradation of poly-α-deuterostyrene might be predicted. The increased yield of monomer would also be expected since substitution of the tertiary hydrogen atom by deuterium would render intramolecular transfer more difficult.

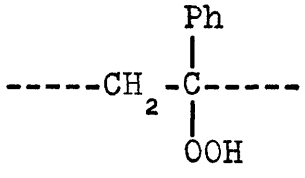
There is thus no conclusive evidence to show that weak links do not exist in polystyrene. It is therefore convenient, at this point, to consider how abnormal structures which might constitute potential weak links can be formed in the polymer molecule.

Jellinek suggests that weak links may be produced by the attack of oxygen on the monomer followed by re-arrangement of the peroxide formed during the polymerisation process (Page.6). If oxygen is involved in weak link formation it is, however, much more probable that it is present in the form of peroxide groups produced by the copolymerisation of oxygen into the polymer chain:-



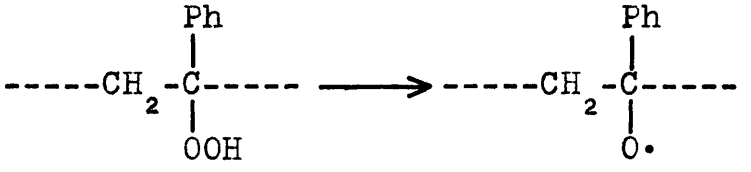
This was suggested as early as 1929 by STAUDINGER[4] who considered such structures might preferentially degrade and thus account for the lower thermal stability of commercial polymers compared with those prepared in the laboratory with the careful exclusion of oxygen.

Peroxide groups produced by oxidation of the polymer would similarly be expected to be less stable than the normal carbon-carbon bond in the polymer chain:-

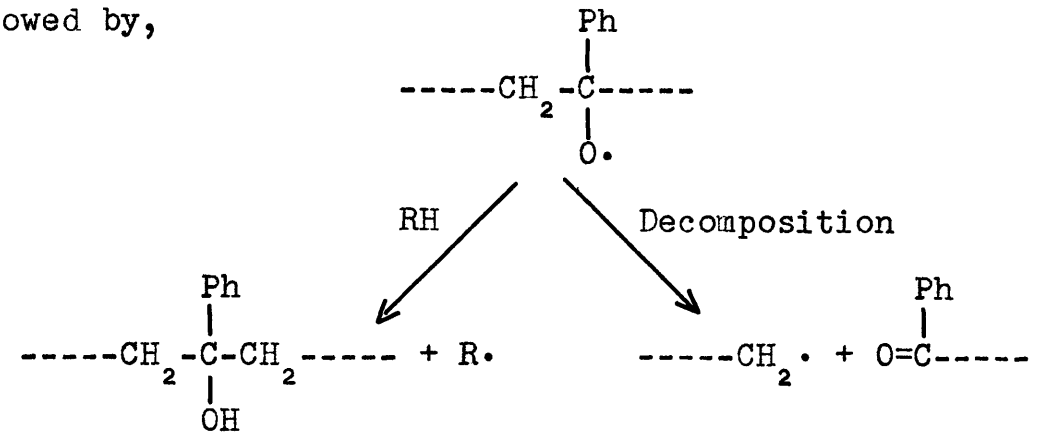


ACHHAMMER, REINEY and REINHART[25] have examined the oxidation of polystyrene, accelerating the process by irradiating the polymer with ultra-violet light. Examination of the infra-red spectra of the degraded polymer shows increased obsorbtion at 3450 cm^{-1} and 1730 cm^{-1}. These bands they attribute to hydroxyl and carbonyl absorbtion respectively which they suggest arises from the decomposition of peroxide groups.

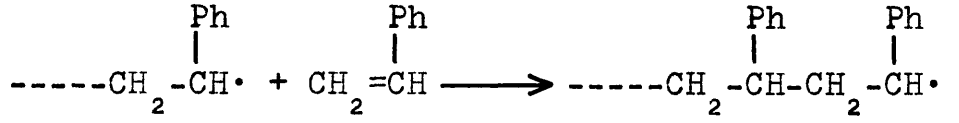
A possible reaction scheme is:-



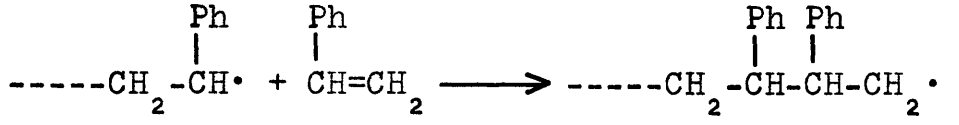
followed by,



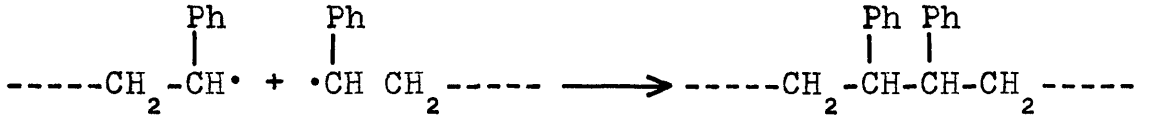
Structures exhibiting a lower degree of thermal stability than the normal carbon-carbon bond in the polymer chain might also arise as the result of some abnormal polymerisation step. The overall structure of the polymer shows clearly that the predominant propagation step is the head to tail addition of monomer units:-



The possibility of head to head addition,



cannot, however, be totally excluded. FLORY and LEUTNER[26] have shown that head to head structures are present in polyvinyl acetate. Further there is much evidence to suggest that termination occurs by combination.[27,28,29]



and therefore each molecule should contain at least one such structure. The bond joining the carbon atoms carrying the adjacent benzene nuclei might be a vulnerable centre for degradation. This may be caused by steric factors alone.

Branching, though reported to be negligible[30,31] may provide yet another source of potential weak links.

If, therefore, the degradation of polystyrene is governed by the presence of weak links it would appear reasonable to assume that the number and existence of such structures may be governed by the conditions of polymerisation. On the other hand if the reaction can be explained by intermolecular transfer alone then this would be expected to be independent of the polymerisation process.

The object of the work about to be described was to re-examine the degradation of polystyrene and from the results to try and distinguish between the two possible reaction mechanisms previously advanced. Because of the possible influence of the conditions of polymerisation on the degradation of polystyrene, the polymers used in the investigation were prepared in the laboratory under carefully controlled conditions which are described in Chapter II. Much of the previous work has been done on commercial polymers[11,17] and it has been

suggested that this might explain certain conflicting features in the results[32]. Whereas previous workers have generally confined themselves to the examination of one feature of the reaction, e.g. decrease in molecular weight or rate of volatilisation, the present work has sought to integrate all the various facets of the process by examining each concurrently with the others.

CHAPTER II.

EXPERIMENTAL TECHNIQUES.

1. The Preparation of Polymers.

It has been pointed out above that much of the difficulty in obtaining a rigid solution to this problem may well be due to the differing modes of preparation of the polymers used. This is especially true where commercial samples are employed since fine control of the polymerisation is not possible and many variables may influence its course which are not known to later workers. In addition, since it has not been fully established at what precise stage the weak links are formed, it is important that as many variables as possible are eliminated from the polymerisation process. The aim of the following experimental techniques was to standardise and thus rigidly control the preparation of the polymers.

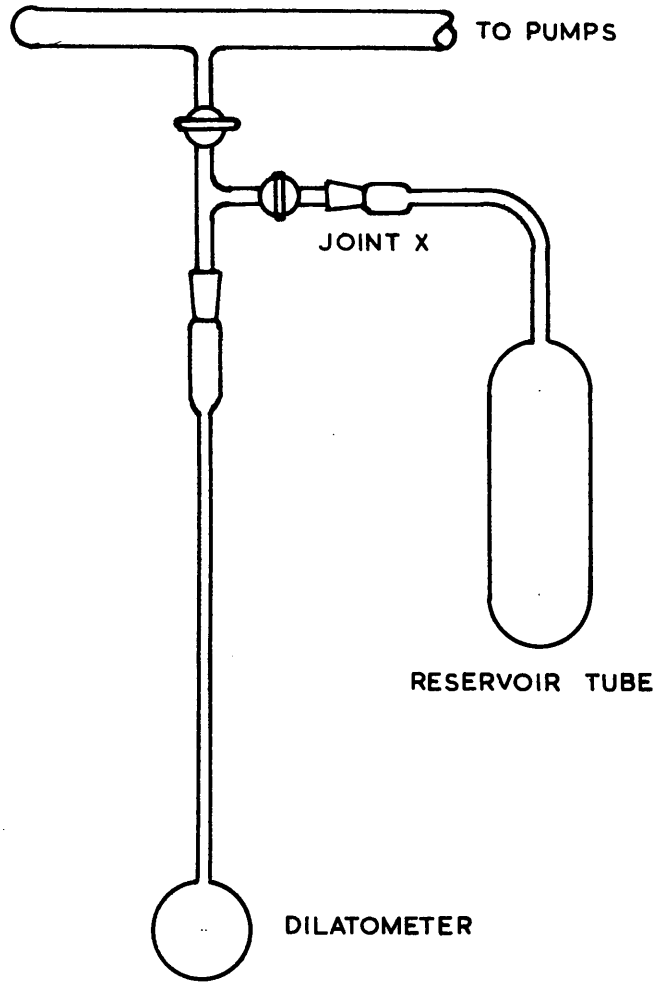


FIG.3.

(i). Purification of Catalyst.

The catalyst used in all cases was benzoyl peroxide (B.D.H. Ltd.) and as supplied contained 30% water. This was removed by dissolving it in the minimum amount of chloroform and after removing the aqueous layer precipitating the peroxide with methanol. The product was then dried in air at room temperature and stored in the dark over calcium chloride.

(ii). Purification of Monomer.

The monomer (Light and Co. Ltd.) was tested for inhibitor with a 0.2N solution of sodium hydroxide. It was found to be free from inhibitor. After standing for forty-eight hours over calcium chloride the monomer was distilled at 37°C and 12 mm. pressure, in all cases the first 20% of the distillate being discarded. This distillation produced a colour free product leaving as residue a straw yellow liquid, the colour being presumably due to the presence of oxidation products of styrene.

(iii). Filling of Dilatometers.

The vacuum system used in the filling of the dilatometers is shown in Fig.3. The monomer was placed in the resevoir tube and frozen using liquid oxygen.

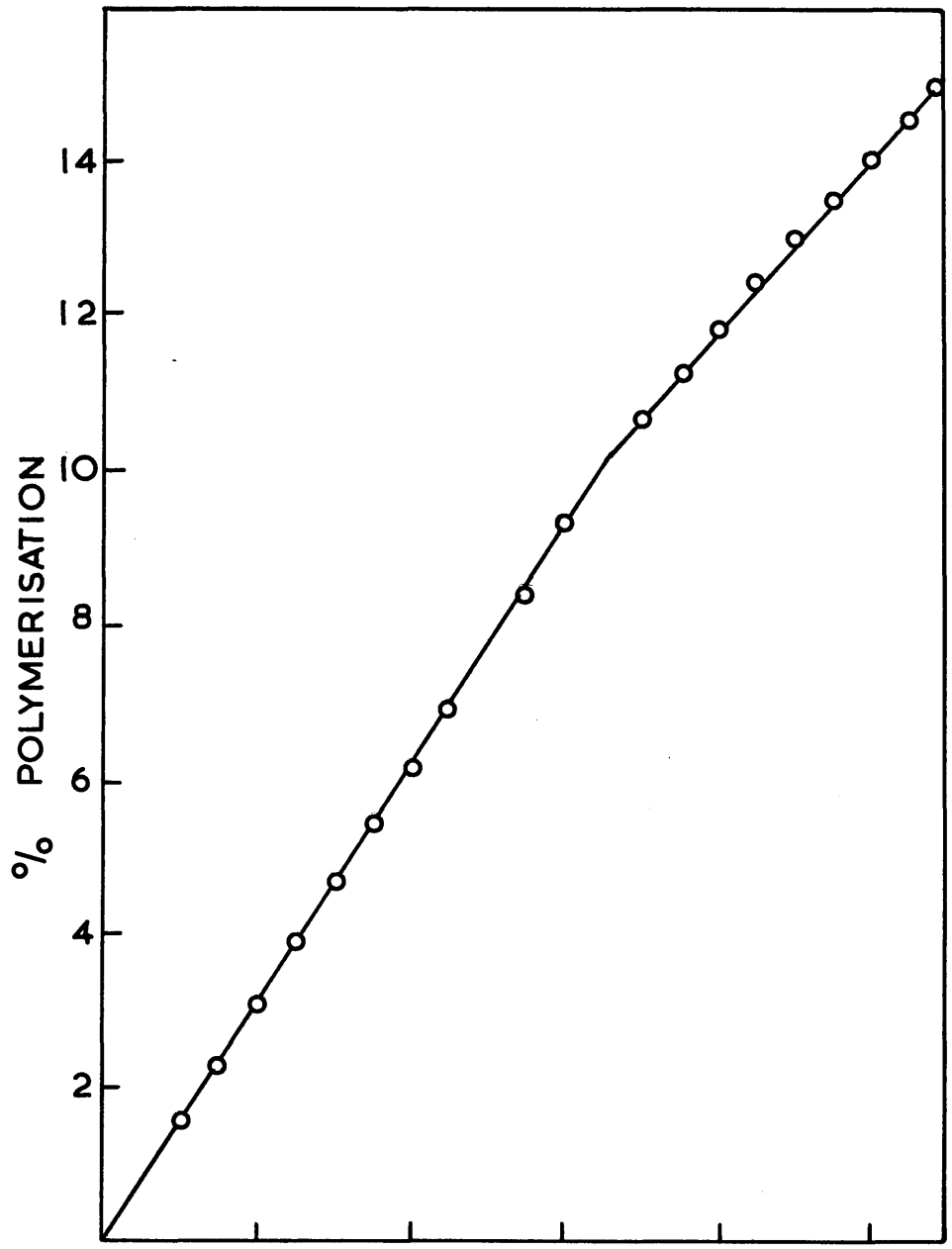
The whole system was then evacuated, a vacuum of the order of 10^{-5} mm. Hg. being provided by a mercury diffusion pump backed by a rotary oil pump. The styrene was degassed three times by freezing and thawing in the usual manner and an initial 20 ccs. distilled off before filling the dilatometer.

It was found that the styrene polymerised in the resevoir tube during the distillation forming a surface film of polymer, which hindered or prevented distillation. In the apparatus shown the joint X enabled the resevoir tube to be rocked, thus providing a safe and convenient method of breaking the film. In this way constant distillation could be ensured. When the required amount of monomer had been distilled in, the dilatometer was sealed under vacuum.

Catalyst, when required, was introduced into the reaction vessel in benzene solution, the solvent being removed under vacuum.

(iv). Polymerisation.

The polymerisations were carried out in a water bath controlled to $\pm 0.01°C$ by a Sunvic H.V.S. Relay and a mercury-toluene regulator. The expansion of monomer and its subsequent contraction on polymerisation were



POLYMER S.6.

FIG.4.

calculated from the data of MELVILLE and VALENTINE[33], a linear relationship being assumed between percentage contraction and temperature of polymerisation.

In the case of U.V. initiated polymerisation the monomer was exposed to radiation from a 125W Osram Mercury Vapour Lamp, the radiation being transmitted through a silica glass window fitted to the water bath.

A typical curve of percentage polymerisation against time is shown in Fig.4. The decrease in rate of polymerisation at about 10% conversion has previously been reported and commented on[33].

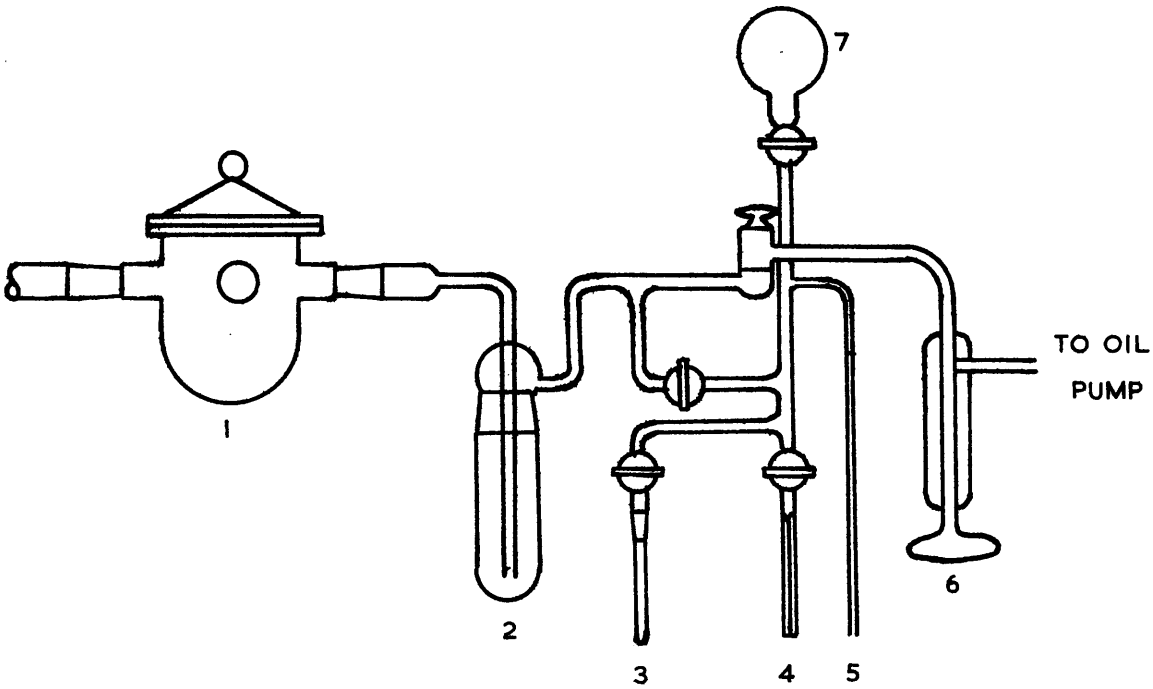
(v). Precipitation of Polymers.

The polymer-monomer mixture on removal from the dilatometer was dissolved in an equal volume of benzene, and the polymer precipitated from this solution by pouring it into methanol. After this process had been repeated to ensure the removal of monomer, and catalyst where present, the precipitated polymer was allowed to dry overnight at room temperature.

It was found that neither direct precipitation of the polymer by methanol from a benzene solution, nor freeze-drying by removing the benzene under vacuum from a frozen solution of the polymer, gave a product which could be ground and seived.

Of the solvents available for polystyrene dioxan proved to be the most satisfactory for precipitation. The method employed was to stir the methanol rapidly using a mechanical stirrer and to add a very dilute dioxan solution of the polymer from a burette. The success of the method depended upon both the dilution of the polymer solution and the rapidity of stirring the precipitant. When the process was successful a dilute milky solution was obtained in which the individual particles of the precipitated polymer were indistinguishable. Aggregation of the precipitated polymer, due in most cases to the dioxan solution being too concentrated, gave a product which after filtration and drying could not be ground.

Following precipitation the polymer was filtered and dried under vacuum for forty-eight hours to remove surface volatiles. It was then ground and seived through a forty mesh copper gauze. In this form the polymer was used for degradation experiments.



DEGRADATION APPARATUS.

1. THE STILL. 2. LIQUID QXYGEN TRAP. 3. MONOMER TUBE.
4. CALIBRATED CAPILLARY. 5. MANOMETER. 6 MERCURY PUMP.
7. EXPANSION FLASK.

FIG.5.

2. The Degradation of Polymers.

Degradation experiments were carried out in a modified form[34] of the dynamic molecular still described by GRASSIE and MELVILLE[10]. This type of apparatus allows the polymer to be degraded in vacuo, thus avoiding the complication of oxidative side reactions which would alter the course of the degradation[9,11], while at the same time facilitating the rapid removal of volatile products from the reaction zone. The design of such an apparatus can be adapted to the needs of the problem under consideration and in this case a section was constructed to enable the products of degradation, volatile at room temperature, to be identified from vapour pressure measurements and to be quantitatively estimated by distillation into a calibrated capillary.

The glasswork of the apparatus is shown diagramatically in Fig5. The still, specially constructed by Quickfit Ltd., consists of a cylinder (Internal diameter 12 cms.), rounded at one end and closed at the other by a dessicator lid sitting on a ground glass flange. The furnace used to degrade the polymers was supported inside the still on a glass stand, the necessary electrical connections being led to the furnace through a manifold fixed into one of the four B.24 sockets on the side of the

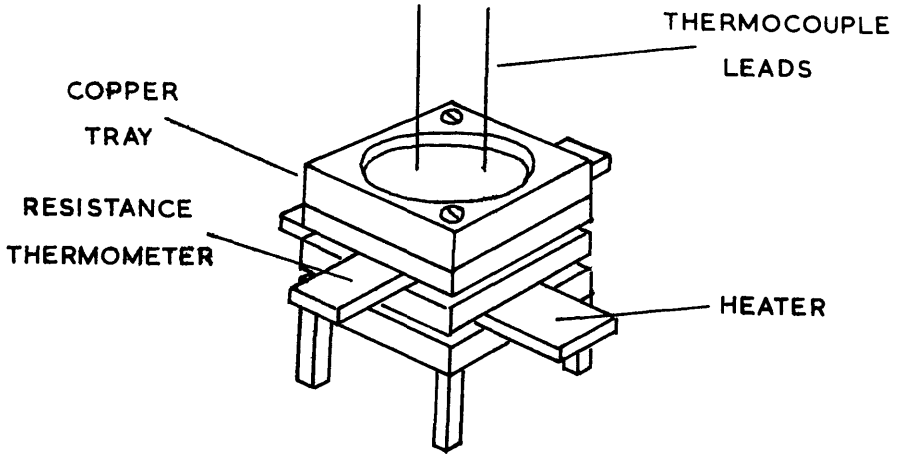


FIG. 6. FURNACE CONSTRUCTION.

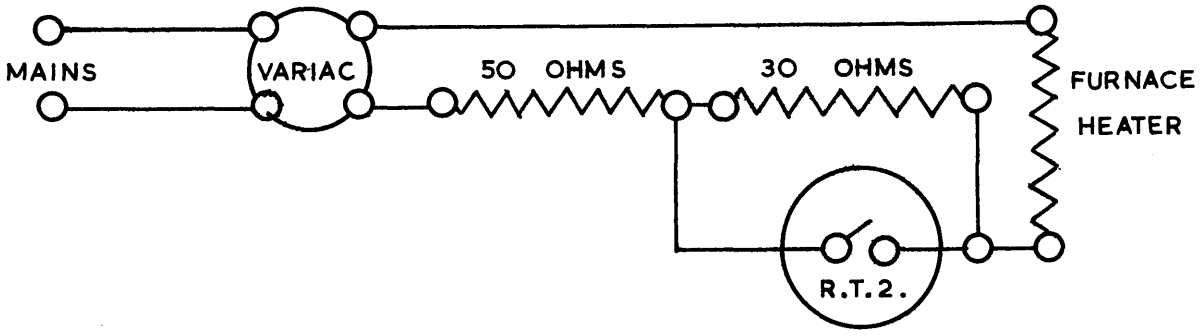


FIG. 7. FURNACE CIRCUIT.

still. Vacuum tight glass to metal seals for these connections were obtained by using borated copper wire.

(i). Furnace Construction.

The heater unit, Fig.6 was made from three copper plates 37 mm. square and 2 mm. thick. A non-inductively wound platinum resistance thermometer (10 ohms), insulated by means of mica sheet, was clamped by screws between the upper two plates. The heating element wound from wire capable of carrying 1.5 amps and having a total resistance of 28 ohms, was held in a similar manner between the lower plates. Connections between the furnace assembly and the wires leading out of the still were provided by screwed sleeve connectors.

(ii). Furnace Control.

One of the major difficulties with an apparatus of this nature is the accurate control of the furnace temperature over long periods of time. This is rendered much more difficult in the present instance as a result of the small heat capacity of the furnace to be thermostated, especially since heat losses are negligible because of the high vacuum conditions. Accurate control to within $\pm 0.5°C$ was however obtained using a Sunvic Resistance Thermometer Controller Type R.T.2. in association with the platinum resistance thermometer. The furnace circuit

incorporating the R.T.2. is shown in Fig.7. The technical details of this instrument need not be dealt with here in detail and it will be sufficient to point out that it functions effectively as a switch, short circuiting the 30 ohm resistance. The control of the furnace depends on the ratio of high to low current as the switch closes and opens. Because of the conditions under which the furnace was operating departure from the recommended ratio had to be made and a suitable ratio was found to be High = 33 V, and Low = 21 V.

(iii) Degradation Tray and Thermocouple Circuit.

The copper tray in which the polymer was degraded was 37 mm. square and 7 mm. deep. A circular hole of about 32 mm. diameter and 4 mm. deep was bored in the centre and onto the surface of the tray was soldered a copper-constantan thermocouple. (See Fig.6). The copper tray during degradations was screwed firmly to the surface of the heating block.

The temperature during degradation could be read accurately to within 0.5°C using a calibrated millivoltmeter and a thermos flask of melting ice as the cold junction of the thermocouple.

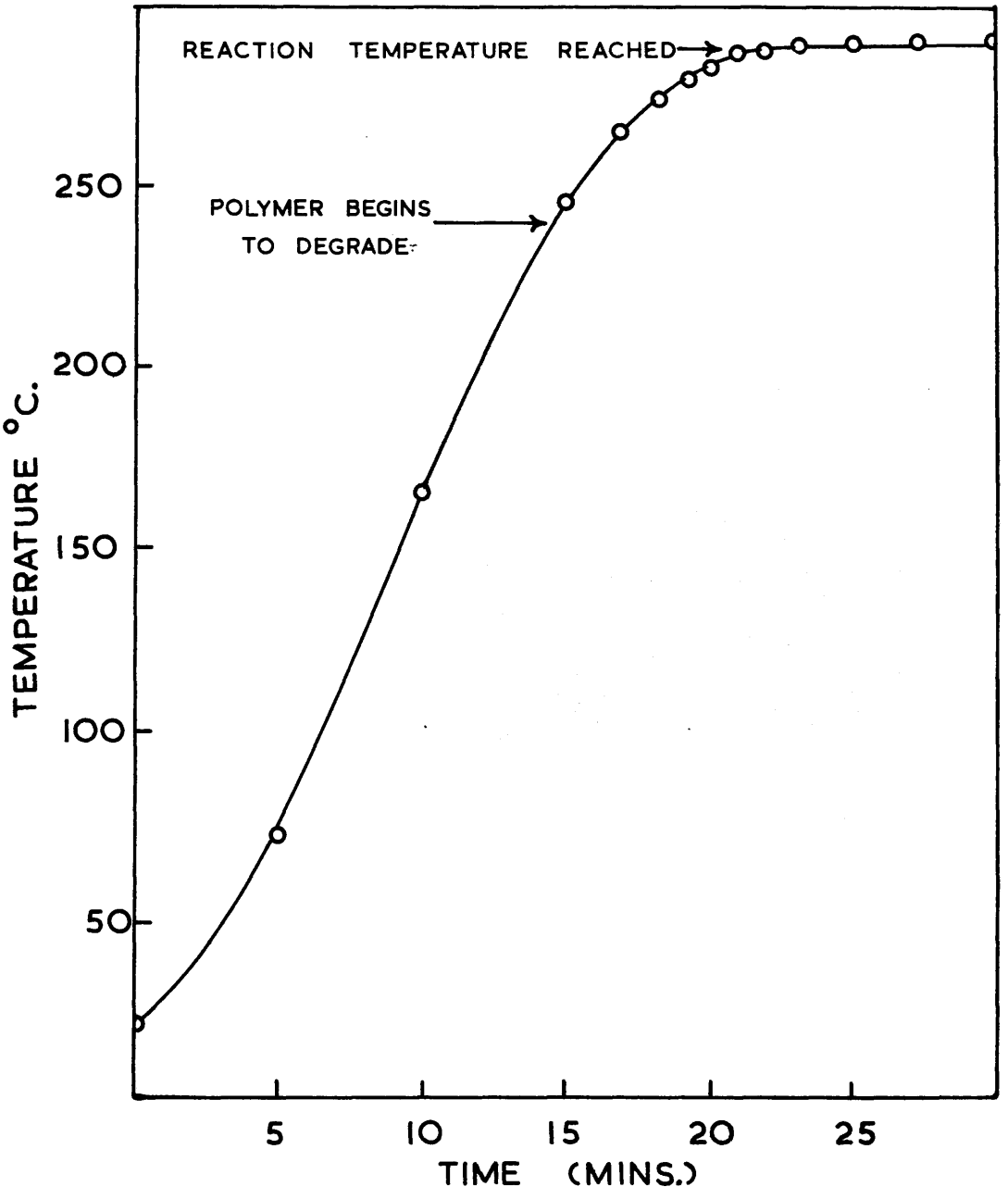


FIG.8. RATE OF HEATING OF FURNACE.

(iv). Efficiency of The Heater.

The conditions under which polymer can be successfully degraded using this apparatus have already been fully discussed by GRASSIE and MELVILLE[10]. The amount of polymer used in the tray for the experiments under discussion here was between 0.25 gm. and 0.30 gm.

The copper powder used to cover the polymer in the tray to produce uniform heating of the sample, was prepared by reducing precipitated copper (Hopkin and Williams Ltd.) in a stream of coal gas, the surface film of oxide being thus removed to give a brick red product.

It is essential in problems in which rate measurements are made that not only is the temperature of reaction maintained constant but also that the temperature is rapidly attained, particularly when the reaction under discussion is initiated at temperatures considerably below those at which measurements are to be made. With the heater described above a temperature of 290°C could normally be obtained in 20 to 25 minutes. Polystyrene begins to degrade at about 240°C so it can be seen from the curve in Fig.8 that the polymer has been degrading for about eight minutes before the reaction temperature is reached. Any error so produced is however negligible in

relation to the periods of degradation employed as in this time something considerably less than 0.06% volatilisation would have occurred. The efficiency of the system may therefore be regarded as satisfactory.

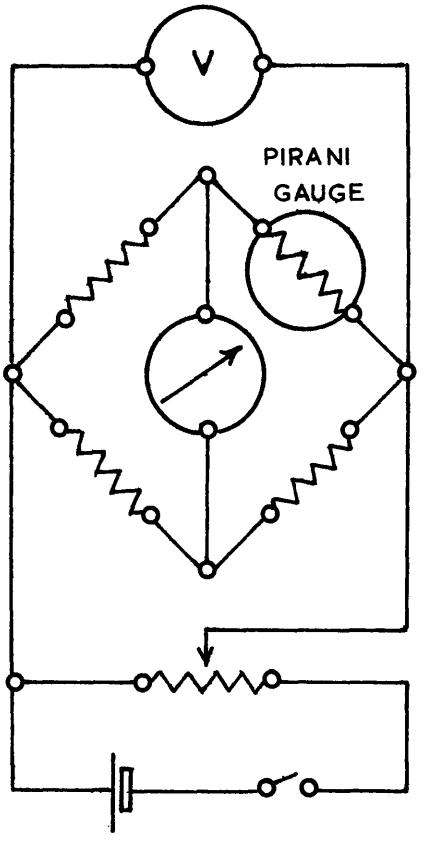
(v) The Estimation of Volatile Material Produced on Degradation.

Of the volatile products formed during the degradation of polystyrene in vacuo only 42% is monomer. The remaining 58% has an average molecular weight of 264 and analysis has shown this to contain dimer, trimer, tetramer and pentamer.[13,15,16] These two fractions can however be separated since the non-monomeric material is involatile at room temperature.

Volatile material produced during degradation in the still (1), (Fig.5), is condensed in the liquid air trap (2). The amount of material collected can then be estimated by distillation at room temperature, into the calibrated capillary (4).

During the degradation of polystyrene in this apparatus a wax-like deposit formed on the sides and lid of the still showing that much of the volatile material did not reach the liquid air trap. This was presumed to be the non-monomeric fraction referred to above.

The total extent of volatilisation was obtained by weighing the tray before and after degradation. Therefore if it could be established that the fraction of volatile products collected in the capillary was monomer, uncontaminated by material of higher molecular weight, the ratio of non-monomeric to monomeric material at any extent of volatilisation could be determined. The most rapid and convenient method of analysing such products is to measure the vapour pressure of the liquid. This was done in the present instance by expanding the unknown into the flask (7) and measuring the pressure recorded on the manometer (5). The volume above the capillary was pumped out, monomer previously degassed in tube (3) expanded in turn, and the pressure measured. The pressures were found to be the same showing the presence of monomer. By repeating this procedure the vapour pressure of the unknown could be measured until the material was exhausted. In this way the fraction was found to be entirely monomeric in nature.



PIRANI GAUGE CIRCUIT.

FIG.9.

(vi) Measurement of The Rate of Volatilisation.

A Pirani Gauge was incorporated into the apparatus and was accommodated in a B.24 side arm fixed into the wall of the still. (See Fig.5). The pressure at any instant in the still is proportional to the expression $(V^2-V_o^2)/V_o^2$ (Where V is the voltage across the bridge when balanced at any pressure, and V_o the voltage when balanced at zero pressure). The electrical circuit used in conjunction with the gauge is shown in Fig.9.

The rate of production of volatile material during degradation can therefore be measured in terms of the pressure set up in the still and can be recorded simply by measuring the balanced voltage in the Pirani Circuit. For quantitative application a careful calibration of the gauge must be made, since the expression $(V^2-V_o^2)/V_o^2$ is only linear with the rate of flow of volatile material through the still within certain limits. In the present instance, however, as the gauge was only required to determine the extent of volatilisation at which the maximum rate of reaction occurred an accurate calibration was unnecessary and a linear relationship was assumed between $(V^2-V_o^2)/V_o^2$ and the pressure in the still. The area under the curve of $(V^2-V_o^2)/V_o^2$ against time, was equated to the loss in weight of the tray during degradation

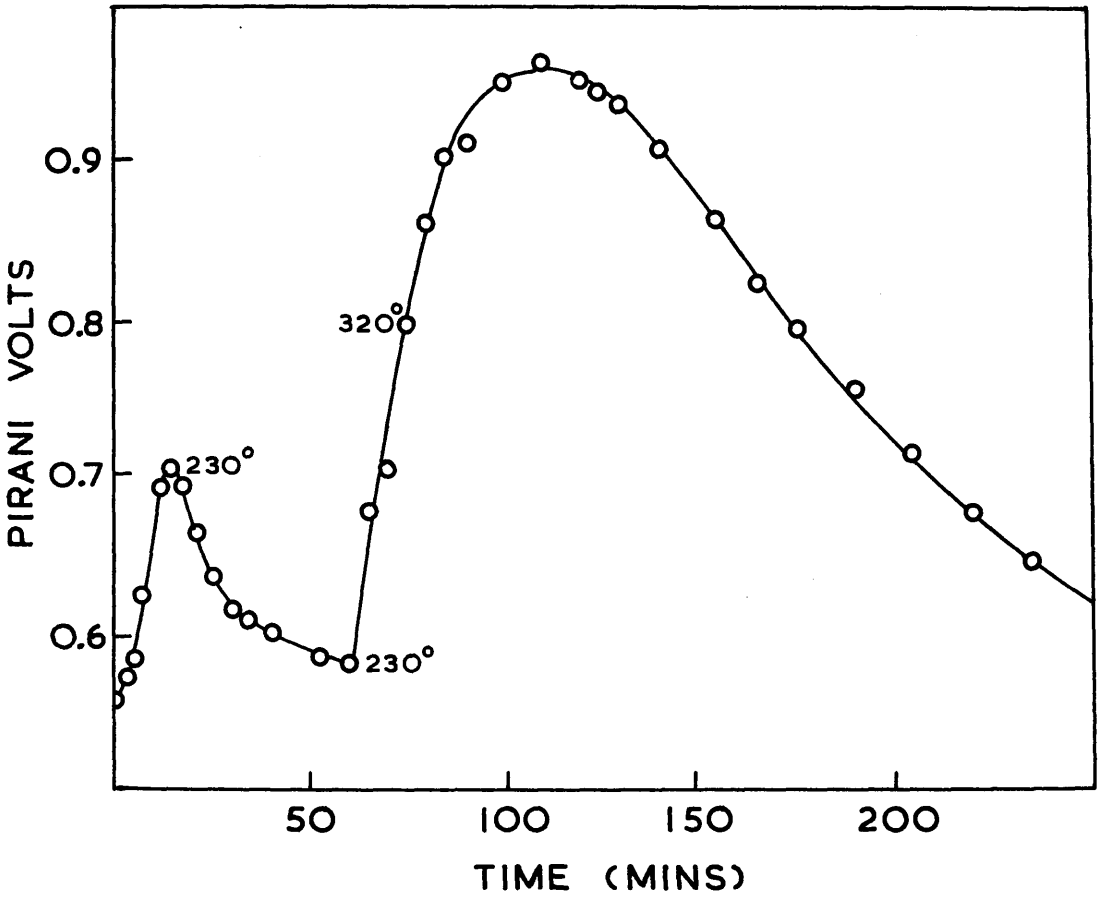


FIG.10. POLYMER S.3. RATE OF VOLATILISATION.

and a graph of rate against percentage volatilisation could then be constructed. From this the point of maximum rate was deduced.

A typical curve of Pirani voltage against time is shown in Fig.10. Here the polymer was heated to 230°C and maintained at that temperature till the Pirani voltage had returned to its zero value. This eliminates the volatile material occluded in the polymer during the precipitation process, which can only be removed by melting the polymer. Thereafter the temperature was raised rapidly to 320°C and the rate of volatilisation followed at that temperature.

(vii) Estimation of Volatiles Occluded in The Polymer.

The existence of volatile material occluded in the polymer makes it necessary to apply a small correction to the extents of volatilisation recorded during the degradation process. This was most easily done by the method indicated above, namely to heat the polymer to 230°C and maintain it at that temperature till the Pirani indicated that all the volatiles had been removed. The difference in weight of the tray before and after heating gave an accurate measure of the volatiles present.

(viii) Temperature Range Employed in Degradation Experiments.

It has already been pointed out in Chapter I that the principal feature of the degradation of polystyrene is the rapid fall in molecular weight during the initial stages of the reaction. The temperature range chosen for study was 280°C to 300°C as this allowed the initial fall in molecular weight to be followed with a certain degree of accuracy while allowing large extents of volatilisation to be reached in a reasonable time. The rate of volatilisation within this range is however too small to be recorded accurately by the Pirani Gauge and it was found that the reaction temperature had to be raised to 320°C to obtain significant results.

3. Measurement of Molecular Weights.

The number average molecular weights of the polymers were measured using a modified form of the Fuoss-Mead Osmometer with a bacterial cellulose membrane.[35] The osmometer was thermostated by water jackets through which water was pumped at constant speed from a thermostat, controlled to $\pm$0.01C° by a mercury toluene regulator and a Sunvic H.V.S. Relay. All measurements were carried out at 25°C using benzene as solvent and under these conditions the osmometer showed a cell constant of -0.03 to -0.04 cm.

Before each measurement was made the osmometer was washed out six times with solvent and then six times with the solution under examination. The static method of recording the osmotic pressure was employed throughout this work and the concentrations of the solutions were measured by running about 10 ml. of the solution from the cell face into a weighing bottle, and then evaporating the solvent in an air oven for sixteen to twenty hours at 110°C.

GRASSIE has pointed out that the occlusion of volatile material within some polymers may cause an error of 5 to 10% in concentration determinations of high polymer solutions.[36] The estimation of volatile material occluded in polystyrene by the method described on page 32 showed that this amounted only to 1%. Therefore, provided all the surface volatiles can be satisfactorily removed at 110°C in the time indicated, measurement of concentrations should be accurate to within this limit. This was confirmed by heating 10 ccs. of a solution containing 0.5 gms. of polymer per 100 gms. of solution under the above conditions, and determining the concentration after 17, 34, and 51 hours. No decrease in the concentration noted after 17 hours heating could be detected and the method was therefore considered satisfactory.

For the determination of undegraded molecular weights solutions containing 0.5 gms. of polymer in 50 ml. of benzene were used. Lower concentrations were obtained by dilution. In the case of polymers which had been degraded the polymer residue was extracted from the copper tray by allowing it to dissolve overnight in benzene at room temperature. The copper was then filtered off and osmotic pressure measurements taken after making the solution up to 50 ml.

The benzene used in these estimations was dried over calcium chloride and distilled through a spiral fractionating column. In all cases the first 25% of the distillate was discarded before collection of the solvent was commenced.

4. Interpretation of Molecular Weight Data.

Benzene has been little used as a solvent for polystyrene in osmotic pressure studies. Its choice as solvent for molecular weight determinations in the work described here was largely determined by the linear relationship existing between π/C and C for polystyrene-benzene solutions, where π is the osmotic pressure and C the concentration of the solution.[37,38] The linear form of the plot is particularly useful especially since the

amount of material remaining as the result of degradation may be as small as 0.15 gm., giving 0.3 gm./100 gms. of solution as the maximum concentration available using the technique outlined above. This normally allows only two dilutions and had the plot been other than linear the validity of any extrapolation would have been subject to considerable doubt.

The molecular weights of the polymers were obtained by applying the Van't Hoff Equation at infinite dilution. Any error introduced by the assumption that the density of the solution was the same as that of the solvent (0.88 gm./cc. at 25°C), was considered negligible and therefore where the osmotic pressure π is measured in centimetres of benzene and the concentration of the solution C in gms./100 gms. of solution, the molecular weight, M, of the polymer is given by:-

$$M = \frac{10330 \times RT}{\underset{C \to 0}{\pi/C}}$$

where R is the Gas Constant and T is the Absolute Temperature. This leads to the more readily applicable expression:-

$$\log M = 5.4025 - \log \underset{C \to 0}{\pi/C}$$

The linear relationship between π/C and C may be expressed by the equation:-

$$\pi/C = \frac{RT}{M} + B.C$$

According to the Flory-Huggins Theory, [39,40] which has done much to increase our understanding of polymer-solvent systems, the slope B of the π/C-C plot is given by $\frac{RT}{V_s d^2}(1-U)$ where V_s is the molar volume of the solvent, d is the density of the polymer and U is a term related to the polymer-solvent interaction. The slope of the plot π/C against C is therefore determined by U. While U is primarily determined by the polymer-solvent interaction it would appear that it is also affected by the temperature at which the polymer is prepared, the slope B decreasing as the temperature of polymerisation is lowered.[41,42] The most obvious explanation for the change in B and therefore in the polymer-solvent interaction, is the occurrence of branching, but as this would be expected to decrease at lower temperatures of polymerisation HUGGINS[43] has suggested that conformational changes occurring during polymerisation in the disposition of the hydrogen atom and the phenyl group relative to the plane of the main chain are the most probable cause of the change in B, as these would affect the extent of chain coiling and hence the polymer-solvent interaction.

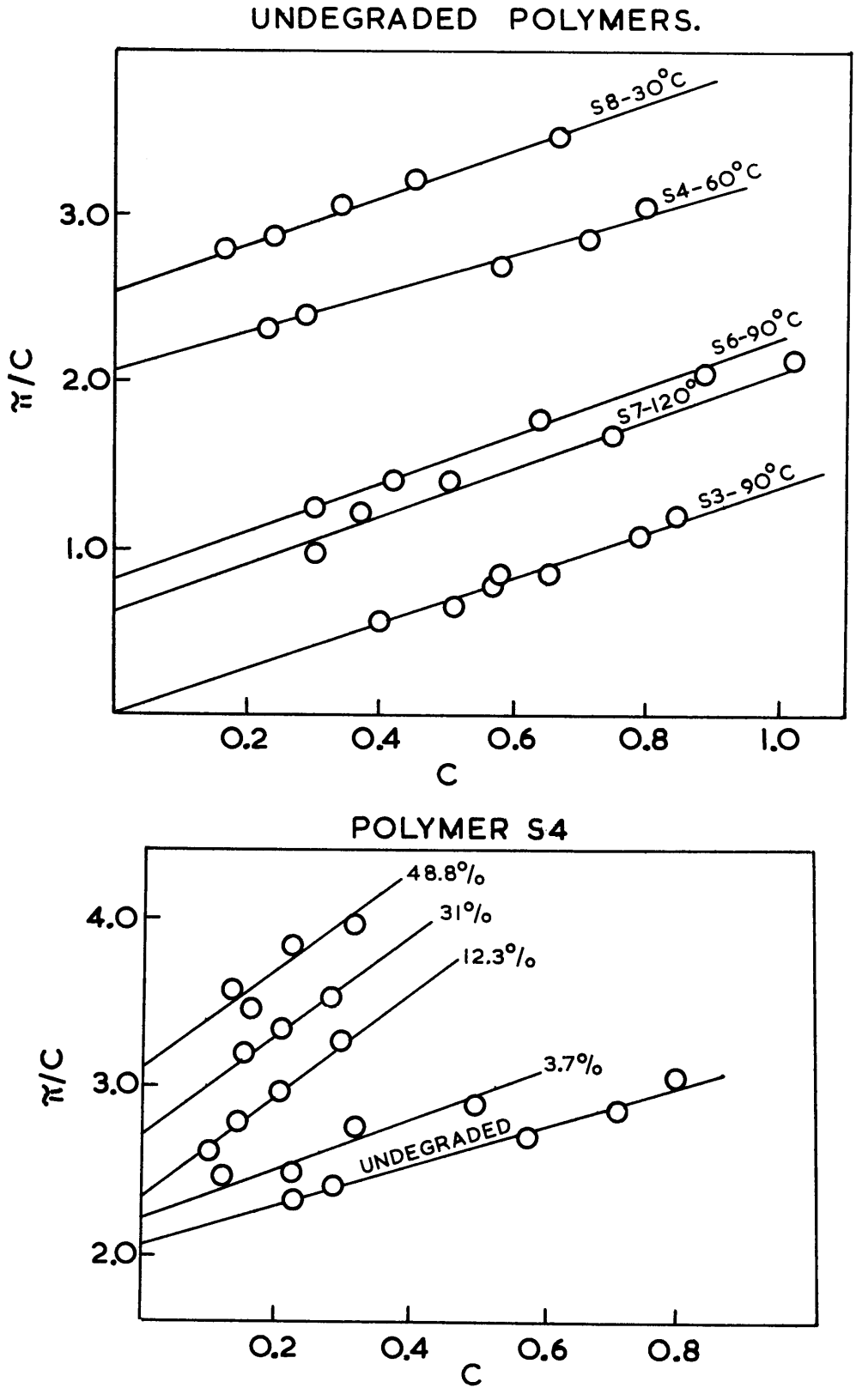

UNDEGRADED POLYMERS.
S8-30°C
S4-60°C
S6-90°C
S7-120°
S3-90°C
3.0
2.0
1.0
π/C
0.2
0.4
0.6
0.8
1.0
C
POLYMER S4
48.8%
31%
12.3%
3.7%
UNDEGRADED
4.0
3.0
2.0
π/C
0.2
0.4
0.6
0.8
C

FIG. 11.

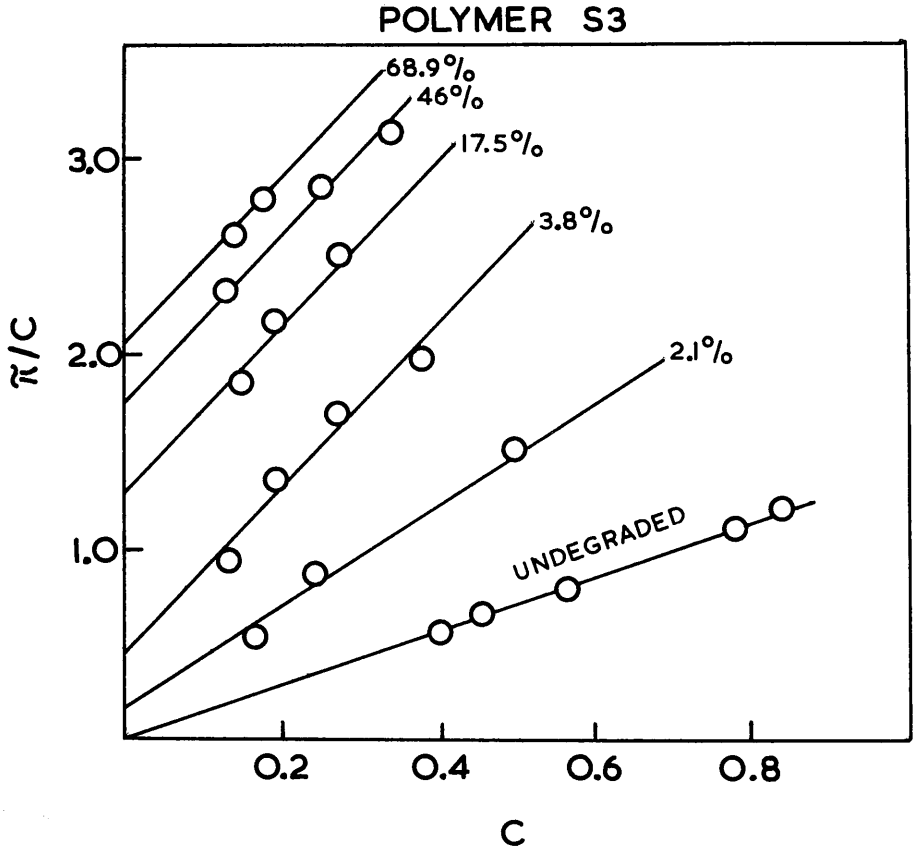


FIG. 12.

When the osmotic pressure data was evaluated for the undegraded polymers employed in the present investigation no general trend in the slope B with the temperature of polymerisation was observed. Details of the preparation of polymers S.3 to S.11 are given in Table II and the osmotic pressure curves of several undegraded polymers are shown in Fig.11.

It was, however, found that the slope of the π/C - C plot for degraded polymer samples differed markedly from that of the undegraded material. Typical results for polymers S.3 and 4 are shown in Figs.11 and 12, where the extents of degradation for the various plots are also given. It will be seen that the slope is variable up to about 5% degradation and thereafter appears to be constant for higher conversions. This result was found to be generally applicable. For large extents of degradation, about 50% or over, where the maximum concentration of polymer available for osmotic pressure determinations is small the slope can therefore be used to determine the molecular weight of the sample by evaluating only one point and using the known gradient to determine the intercept π/C. $_{C\to 0}$

TABLE II

Details of the preparation of polymers S.3 to S.11.

Polymer.	Temp. of Polymerisation	Catalyst Percent. Wt./Vol.	Extent of Polymerisation	Mol.Wt. M_o	Percent Volatiles
S.8	30°C	1.00	15%	99,080	1.67
S.11	30°C	0.30	15%	130,200	3.40
S.4	60°C	0.30	15%	122,700	3.48
S.5	60°C	0.30	5%	332,400	1.06
S.3	90°C	None	15%	10×10^6	1.44
S.6	90°C	0.03	15%	315,800	1.16
S.7	120°C	None	15%	421,000	0.49

Discussion of the theoretical implications of the change of the slope on the basis of the Flory-Huggins Theory is scarcely warranted at the present stage of investigation. The position is extremely complicated in view of the fact that during degradation the polymer molecules are undergoing chain scission and the distribution in the sample is changing at the same time. These results do, however, establish the need to evaluate each π/C-C

plot independently during molecular weight measurements on degraded samples.

CHAPTER III

THE REACTION MECHANISM

1. Change in Molecular Weight During Degradation.

JELLINEK has reported that during the degradation of polystyrene the molecular weight falls rapidly in the initial stages of the reaction to a limiting value which is apparently determined by the degradation temperature (Fig.1)[11]. To account for these results, he has postulated that degradation takes place at weak links which are distributed at random along the polymer chain, and that the reaction occurring at these points is a composite one of chain scission and disappearance of weak links without chain scission. In this way, the varying limiting molecular weights can be accounted for. Neither MADORSKY[17] nor WALL, HART and BROWN[23] have investigated the possible effect of the temperature of degradation on the decrease in molecular weight. These authors chose to express the change in molecular weight during degradation in terms of percentage degradation to volatile material

rather than in terms of time of degradation as Jellinek does. If, however, as Jellinek suggests, weak links can disappear without chain scission, then it is to be expected that the molecular weight-conversion data will also vary with the temperature of degradation. It was therefore decided that the starting point of the present investigation should be a re-examination of the degradation at several temperatures, 280°, 290° and 298°C being the temperatures selected, since within this range the fall in molecular weight could be followed with a reasonable degree of accuracy while relatively large extents of degradation could be obtained within suitable experimental periods. The results for the degradation of polymers S.4 and S.5 at these temperatures are given in Tables III and IV.

TABLE III

Degradation of Polymer S.4

Molecular Weight - 122,700

Temp. (°C)	Time (Hrs.)	Mol.Wt.	% Monomer	% Volatilisation
280	6.0	114,800	1.14	3.73
280	12.0	108,000	3.94	12.26
280	18.0	113,800	4.94	17.81
280	24.0	101,000	8.25	25.89

TABLE III (Cont.)

Temp. (°C)	Time (Hrs.)	Mol.Wt.	% Monomer	% Volatilisation
280	32.0	92,870	-	30.99
280	44.0	81,750	16.67	48.80
290	5.0	106,100	5.71	10.69
290	10.0	94,970	8.66	19.50
290	12.0	92,190	9.53	21.53
290	15.0	100,700	11.00	28.25
290	20.0	-	16.40	39.90
290	22.0	77,500	19.20	53.50
298	1.0	108,000	-	1.25
298	2.5	103,500	3.10	8.32
298	5.0	89,910	9.07	27.16
298	7.0	87,120	11.54	30.25
298	10.0	80,720	23.84	60.88

TABLE IV

Degradation of Polymer S.5

Molecular Weight - 332,400

Temp. (°C)	Time (Hrs.)	Mol.Wt.	% Monomer	% Volatilisation
280	6.0	185,800	2.63	7.06
280	12.0	163,000	5.38	12.02
280	18.0	134,400	7.08	17.16
280	24.0	134,400	8.95	24.19
280	35.0	82,560	18.19	50.27
280	46.0	94,280	21.18	58.42
290	1.5	234,000	-	2.80
290	3.0	157,900	4.41	9.02
290	6.0	128,900	5.14	14.10
290	10.0	111,800	12.36	29.56
290	12.0	111,800	18.70	39.80
290	15.0	90,220	19.99	49.32
298	2.0	119,200	4.43	11.85
298	2.34	108,000	5.67	18.17
298	4.0	103,400	13.14	30.89
298	6.0	103,400	10.46	29.71
298	9.0	88,330	15.00	39.70

POLYMER S4.

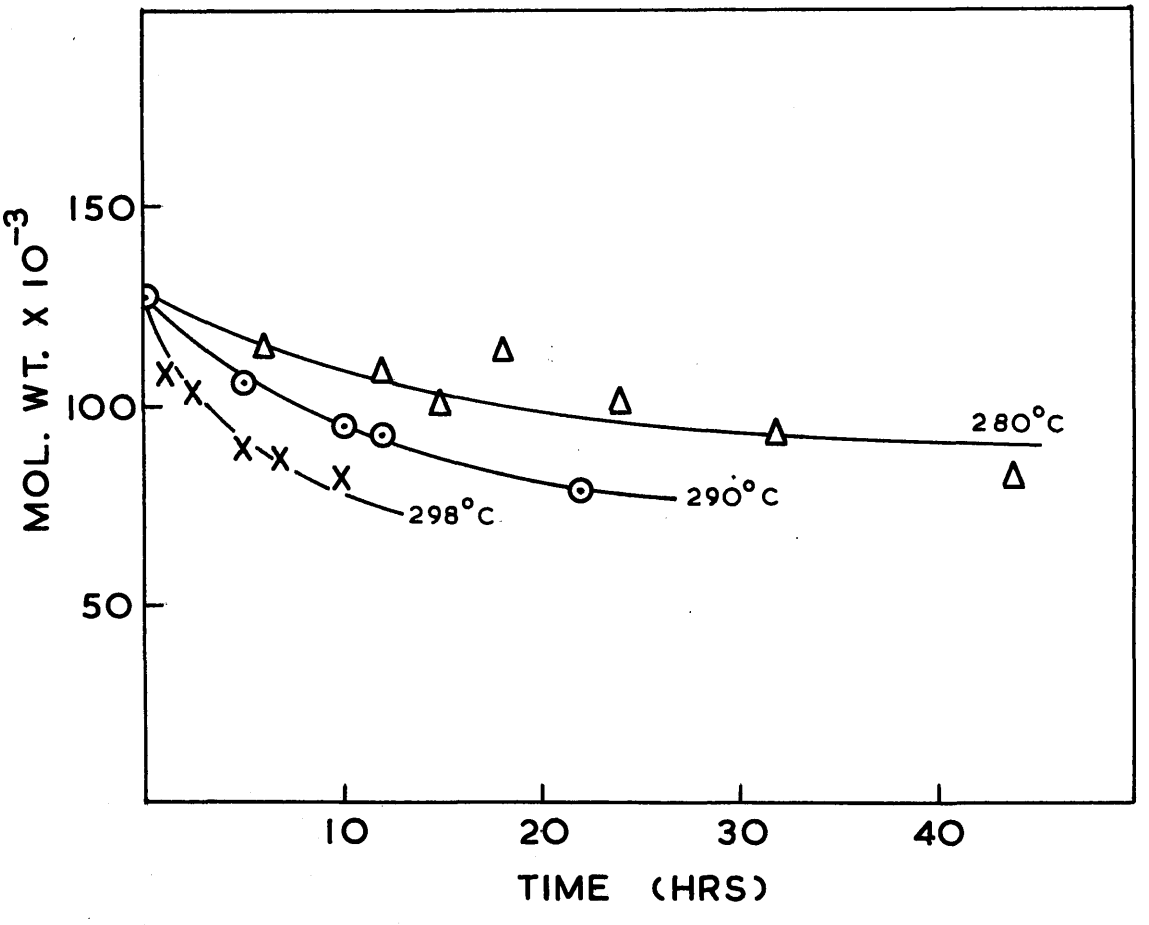


FIG. 13.

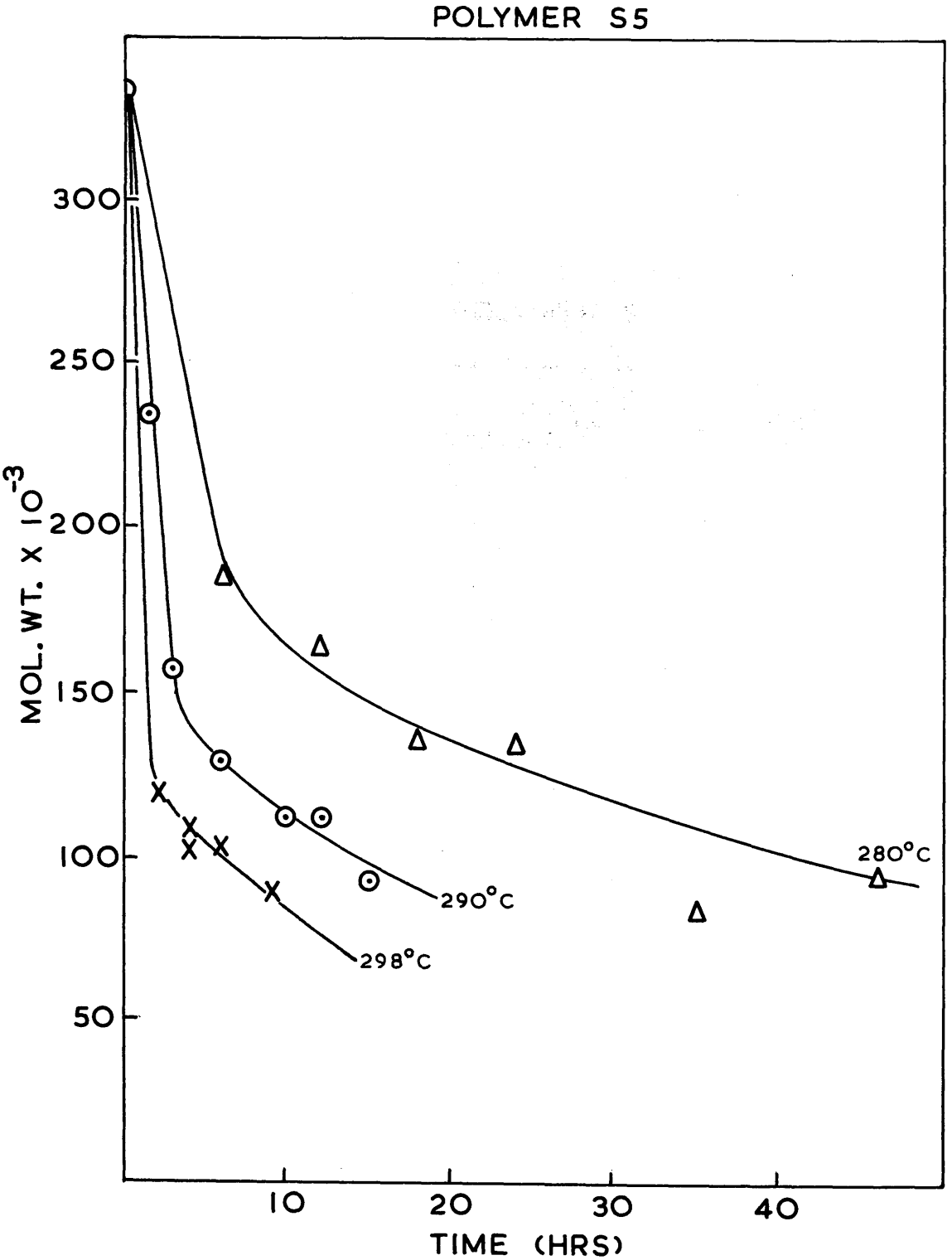

POLYMER S5
300
250
200
150
100
50
MOL. WT. X 10^{-3}
10
20
30
40
TIME (HRS)
280°C
290°C
298°C

FIG. 14.

POLYMER S4.

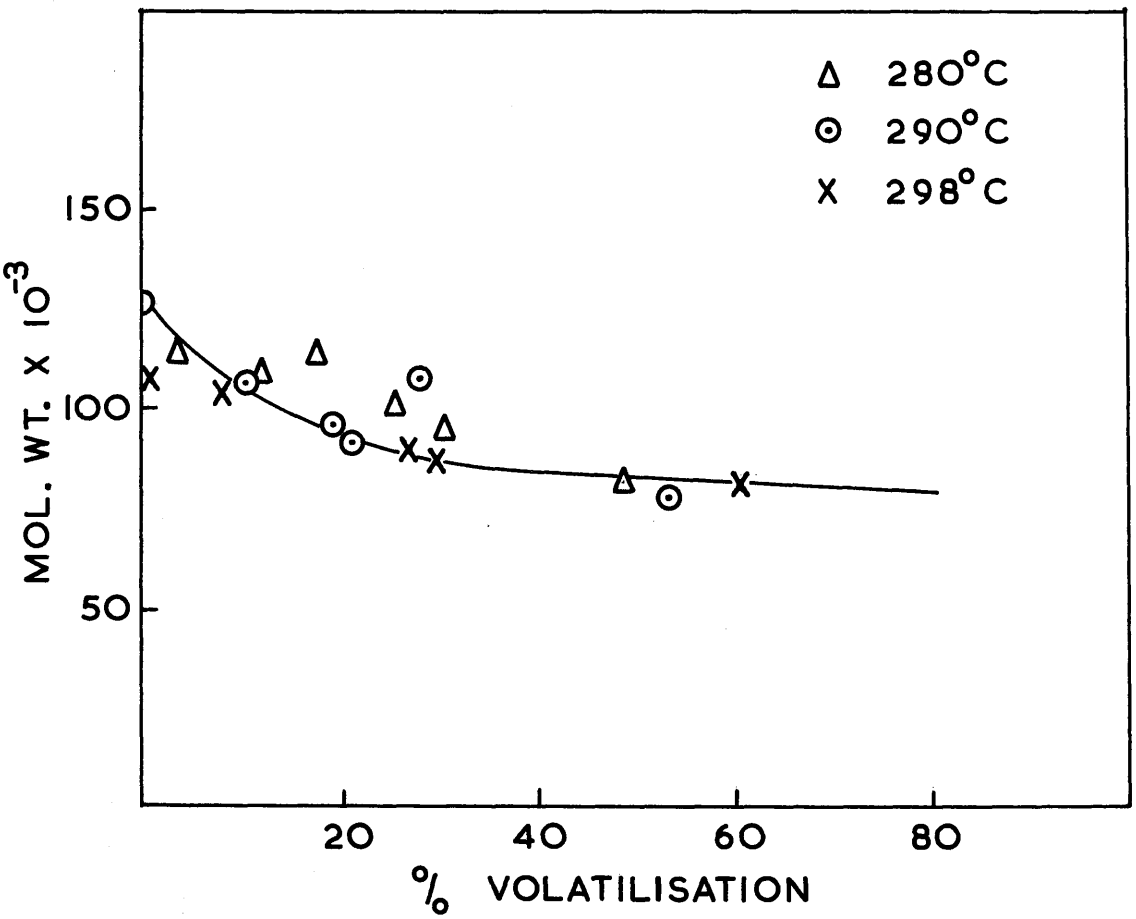


FIG. 15.

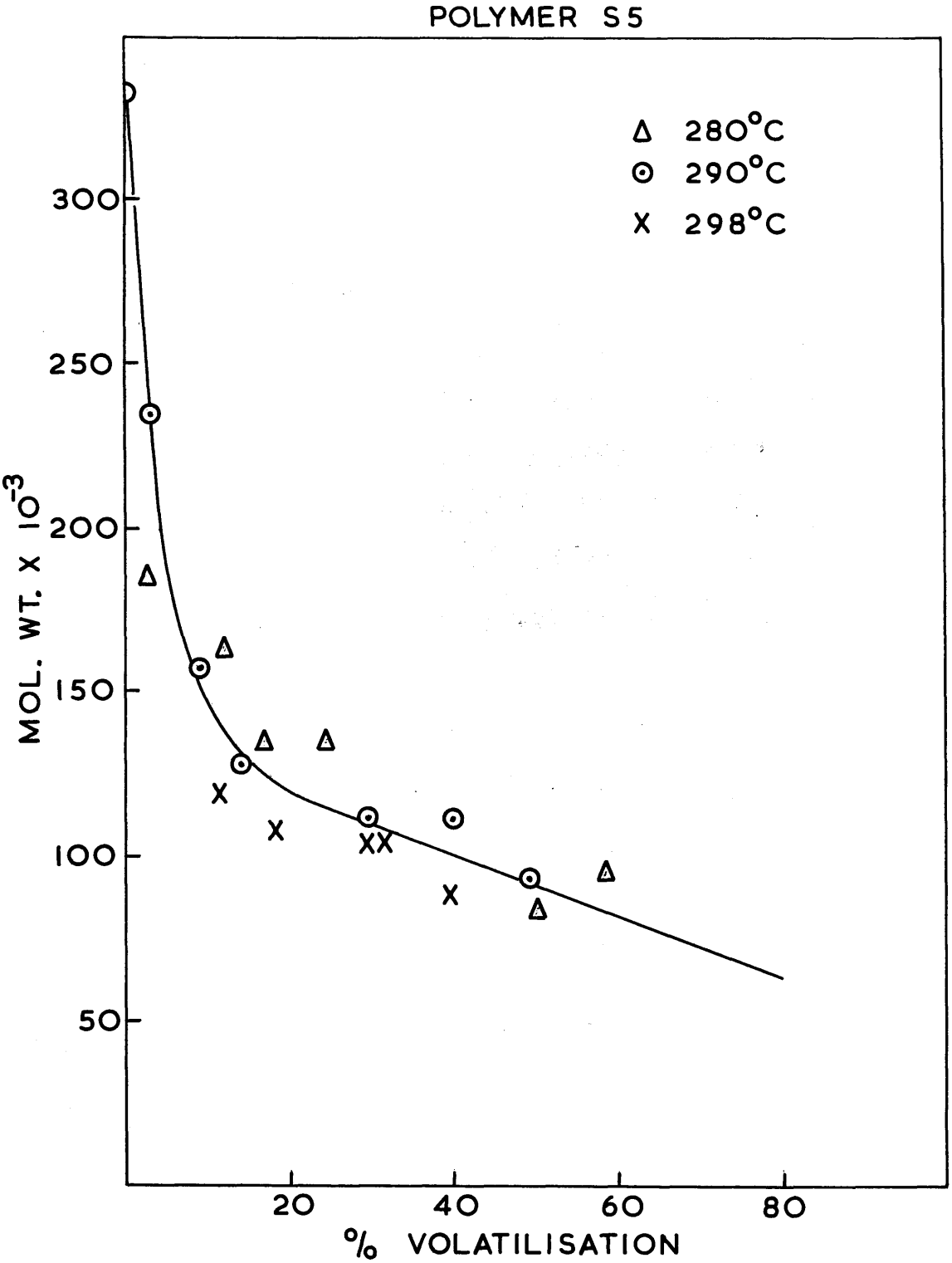

POLYMER S5
Δ 280°C
⊙ 290°C
X 298°C
MOL. WT. X 10^{-3}
300
250
200
150
100
50
20
40
60
80
% VOLATILISATION

FIG. 16.

The molecular weight of the degrading polymers was plotted first against time of degradation and the curves obtained for polymers S.4 and S.5 are shown in Figs.13 and 14 respectively. These are similar to those reported by Jellinek (See Fig.1) in that after a sharp initial decrease, the molecular weight of the degrading polymer falls more slowly. The extent of the fall again appears to depend on the temperature of degradation. When, however, the molecular weight is plotted not against time, but against percentage conversion to volatile material (Figs.15 and 16) an entirely different picture emerges. Irrespective of the temperature of degradation all the points now lie, within experimental error, on the same curve. The small tendency to lower molecular weights at higher temperatures, shown in the case of polymer S.5, in which the molecular weight decrease is large, can be accounted for in terms of the mechanism deduced below as a small increase in the relative rate of chain scission over the rate of production of volatile material. It is thus no longer necessary to assume that weak links can disappear without chain scission and hence the extent of the fall in molecular weight occurring during degradation may be defined by experiments carried out at only one temperature.

From the general shape of the molecular weight-conversion curves, it is apparent that the reaction can be divided into two phases. Up to approximately 30% volatilisation, the predominant reaction is one of chain scission. After this point has been reached, the molecular weight decreases linearly with increasing extents of volatilisation, and here the reaction presumably proceeds through a reverse polymerisation mechanism from the chain ends. Jellinek has suggested that the chain length of this reaction is small and that between five and ten monomer units are split off per chain end formed. SIMHA[44] on the assumption that the rapid decrease in molecular weight is due to intermolecular transfer, and that all volatile products other than monomer are produced in this reaction step, has concluded that the zip length between acts of transfer is of the order of 3. Examination of the molecular weight-conversion data for polymers S.4 and S.5 reveals that the chain length of the reaction is considerably longer than either of these authors suggests. This may be shown directly in the following way.

Chain scission is complete at 30% volatilisation, the point of inflexion in the molecular weight-conversion curves. If the diagonal is drawn from this point to zero molecular weight and 100% conversion, then the approximate

chain length of the reaction under discussion can be deduced from the relationship between the diagonal and the experimental lines.

It has been suggested that degradation within the limits 30 to 100% conversion is initiated at the chain ends and is propagated through a reverse polymerisation reaction. Where the chain length of this reaction is longer than the chain length of the molecule, each chain once activated will disintegrate completely to monomer and the molecular weight during this phase of the reaction will remain sensibly constant. On the other hand, where the chain length of the reaction is less than the chain length of the molecule, then one stable residue will remain for each molecule activated, and the diagonal indicated above will be followed. The average molecular weight to which the polymer degrades by chain scission is given approximately by the molecular weight at 30% conversion. Since the experimental lines for polymers S.4 and S.5 for conversions greater than this lie between the diagonal indicated and the horizontal drawn through the molecular weight curve at the same conversion, it must be deduced that on the average, less than one stable involatile residue remains per act of initiation at the chain ends of the degraded polymer molecules. The chain length of the

reverse polymerisation reaction for polymer S.4 must approximate closely to the chain length to which the polymer degrades since the line drawn through the experimental points lies close to the horizontal.

Only about 40% of the volatile products of degradation is monomer. The remainder is composed of dimer, trimer, tetramer and pentamer, the proportion of the last two present being comparatively small. [13,15,16] Dimer and trimer are present in approximately the same yield.[1,13] Assuming that intermolecular transfer plays no part in the reaction, and that the various non-monomeric products are produced in a reverse polymerisation process by intramolecular transfer, the chain length of the reaction for polymer S.4 may be deduced as being of the order of 600.

2. Production of Volatiles During Degradation.

The relatively high limiting value to which the molecular weight falls, 90,000 for S.4 and 140,000 for S.5, suggests that some chain scission process other than intermolecular transfer is occurring. A continuous decrease to low molecular weights would have been expected had intermolecular transfer played a significant role in the reaction. Further evidence in support of this theory may be obtained from the relative proportions of non-monomer

and monomer produced at various stages during the reaction. In Table V the ratios of non-monomer to monomer for degradations at 280°C and 298°C are quoted.

TABLE V

Ratio of Non-Monomeric to Monomeric Products at 280°C

Polymer S.4		Polymer S.5	
% Volatilisation	Non-Monomer / Monomer	% Volatilisation	Non-Monomer / Monomer
3.73	2.3	7.06	1.7
12.26	2.1	12.02	1.2
17.81	2.6	17.16	1.4
25.89	2.1	24.19	1.7
48.80	1.9	50.27	1.8
		58.42	1.8

Ratio of Non-Monomeric to Monomeric Products at 298°C

Polymer S.4		Polymer S.5	
% Volatilisation	Non-Monomer / Monomer	% Volatilisation	Non-Monomer / Monomer
8.32	1.7	11.85	1.7
27.16	2.0	18.17	2.2
30.25	1.6	30.89	1.4
60.88	1.6	29.71	1.8
		39.70	1.7

In the absence of intermolecular transfer all non-monomeric material must be produced solely by

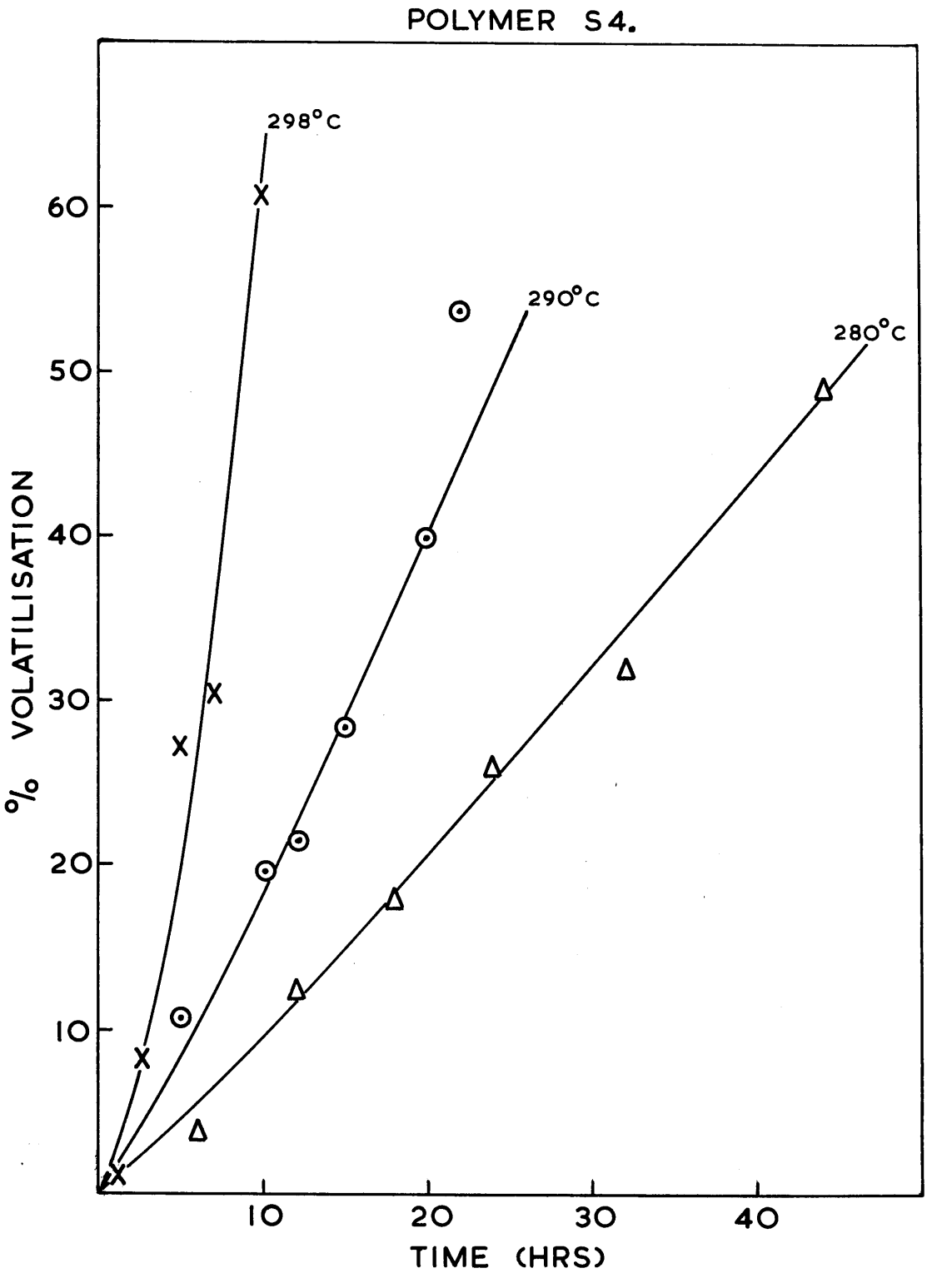

POLYMER S4.
298°C
290°C
280°C
60
50
40
30
20
10
% VOLATILISATION
10
20
30
40
TIME (HRS)

FIG. 17.

intramolecular transfer near chain ends. Under these conditions, the rate of production of non-monomeric and monomeric material will be proportional only to the concentration of free radical chain ends. The ratio of non-monomer to monomer should therefore remain constant throughout the course of the reaction for any one temperature. On the other hand, where intermolecular transfer is included in the reation, the possible formation of non-monomeric material by transfer at or near chain ends cannot be neglected. The rate of production of non-monomeric material would consequently depend not only on the concentration of polymer radicals, but also on the concentration of stable chain ends. The ratio of non-monomer to monomer would therefore increase, particularly in the early stages of reaction where the molecular weight is falling rapidly. Examination of the data in Table V shows that within the limits of experimental error the ratio remains reasonably constant from low to high conversions, and hence the absence of intermolecular transfer may be inferred. Chain scission must therefore occur at weak links present in the polymer molecule.

3. Rate of Production of Volatile Material.

In Fig.17 the curves of percentage volatilisation against time for polymer S.4 are shown.

It can be seen that these are smooth and exhibit no period of inhibition in the initial stages of degradation similar to that reported by JELLINEK.[11] Further, the slight curvature in these lines up to about 25% conversion, shows that the rate of production of volatile material increases early in the reaction. This is in agreement with the results of MADORSKY[17] who reports that the rate reaches a maximum at 30 - 40% conversion. The position of the rate maximum for polymer S.4 cannot, however, be obtained accurately from the conversion-time curves shown, nor is the pressure of volatile products in the still at these temperatures sufficient for the successful application of the Pirani Gauge to rate measurements. Experiment showed that the rate maximum could be accurately defined by increasing the temperature of degradation to 320°C. Since the molecular weight-conversion curve is independent of the temperature of degradation within the range 280° - 300°C it is reasonable to assume that little error will be incurred by applying rate measurements at 320°C to molecular weight data obtained within this range.

A typical Pirani plot obtained during the degradation of polymer S.3 at 320°C is shown in Fig.10. The relationship between the rate of degradation and percentage conversion to volatile material can be derived

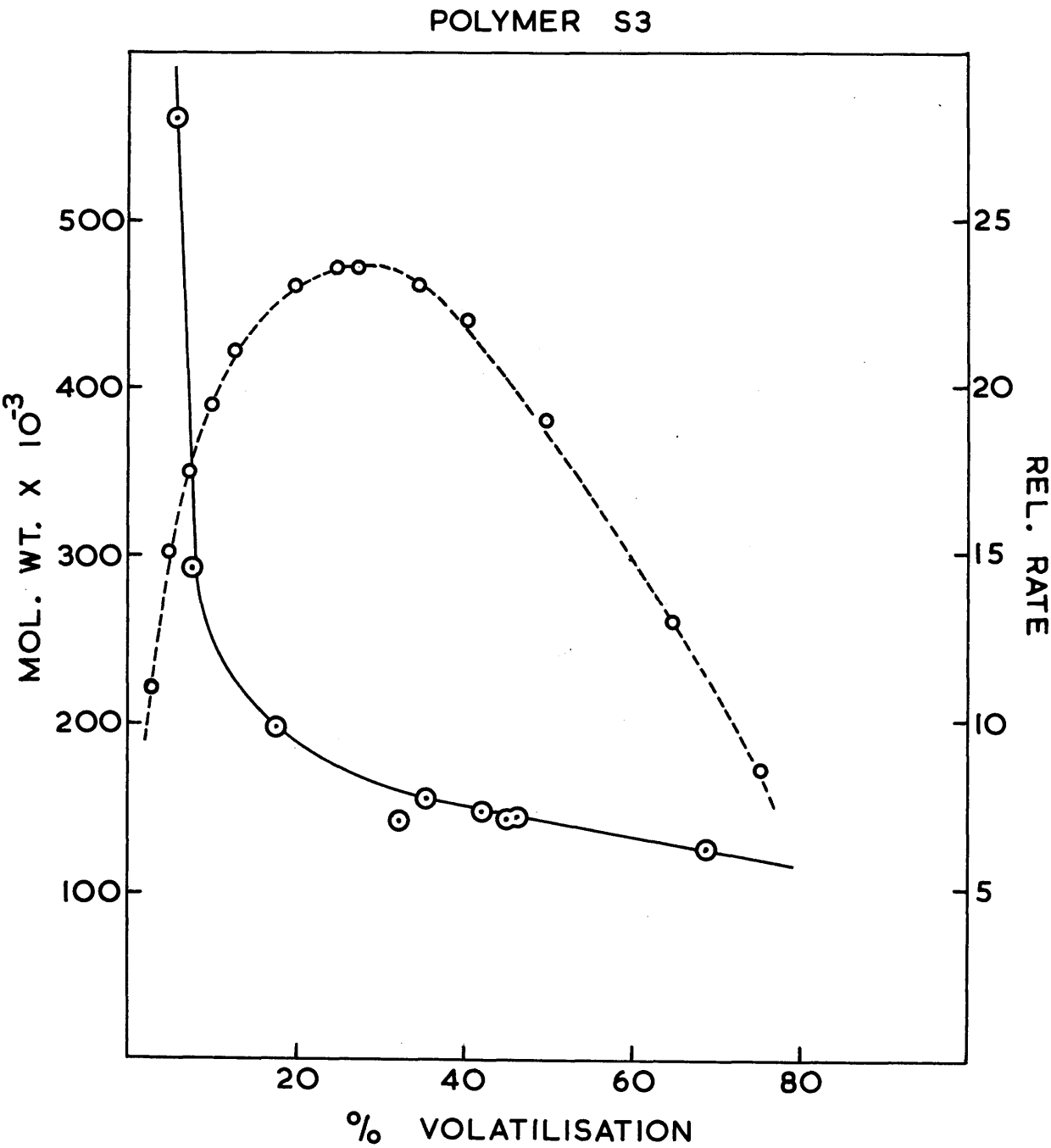

POLYMER S3
MOL. WT. X 10^{-3}
500
400
300
200
100
REL. RATE
25
20
15
10
5
20
40
60
80
% VOLATILISATION

FIG. 18.

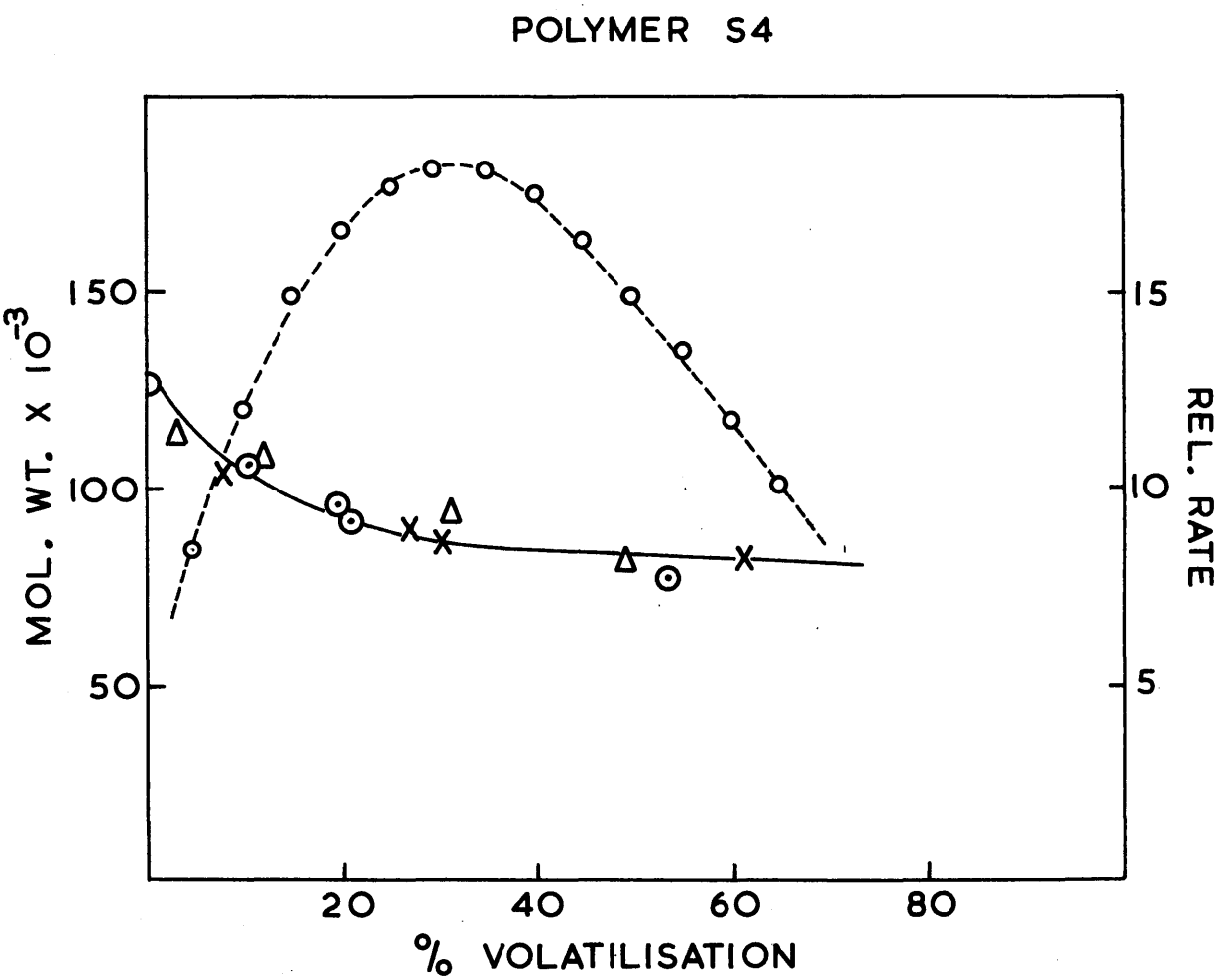

POLYMER S4
MOL. WT. X 10^{-3}
150
100
50
REL. RATE
15
10
5
20
40
60
80
% VOLATILISATION

FIG. 19.

from this curve by the method outlined in the previous chapter (Page 31). In Figs.18 and 19, the curves of molecular weight versus percentage volatilisation and relative rate versus percentage volatilisation for polymers S.3 and S.4, respectively, have been superimposed and the relationship between the fall in molecular weight and increase in rate of production of volatile material can be seen. The relevant data for the degradation of polymer S.3 is given in Table VI.

TABLE VI

Degradation of Polymer S.3

Molecular Weight = 10×10^6 (Approx.)

Temp. (°C)	Time (Hrs.)	Mol. Wt.	% Volatilisation
290	1.0	1,263,000	2.13
290	2.5	561,400	5.94
290	4.0	293,800	7.48
290	6.0	197,300	17.49
290	9.0	141,900	32.28
290	10.5	154,300	35.67
290	14.5	148,600	41.98
290	12.0	141,900	45.10
290	14.0	141,900	46.02
290	15.0	122,700	68.89

It has already been pointed out above that the production of volatile material is initiated at the chain ends and hence the rate of volatilisation will increase with the number present. The increasing rate of production of volatile material up to approximately 30% volatilisation can therefore be adequately explained in terms of the increasing number of degradable chain ends produced by the chain scission reaction. The maximum number of degradable chain ends will be present when the chain scission reaction is just complete, namely at 30% volatilisation, and the occurrence of the rate maximum in the volatilisation curves at approximately the same conversion must be considered very satisfactory.

4. Nature of The Chain Scission Reaction.

Degradation which proceeds through the rupture of a carbon-carbon bond in the main polymer chain will presumably take place by the homolytic fission of the bond concerned. The radicals so produced may then rapidly split off monomer in a reverse polymerisation reaction or may alternatively be stabilised by hydrogen transfer with the resultant production of double and single bond ends. The latter reaction is similar to that occurring in the termination of radicals by disproportionation in polymerising systems. Where chain scission takes place by disproportionation, the production of volatile material will

follow the subsequent breakdown of one or other of the chain ends formed.

A relatively high initial rate of volatilisation would be expected where chain scission results in radical formation and this should rapidly decrease as the weak links disappear. The rate curves for polymers S.3 and S.4 show that this is not the case, and that the rate depends rather on the concentration of molecular ends in the system.

The initial rates to be expected for the production of volatile material by both mechanisms may be calculated approximately on the basis of the following simplified kinetic scheme, which represents the essential features of the depolymerisation reaction:-

		Rate
Initiation	$M_n \longrightarrow P_n$	I
Depropagation	$P_r \longrightarrow M + P_{r-1}$	$k_d(P)$
Termination	$P_r + P_s \longrightarrow M_r + M_s$	$k_t(P)^2$

where M_r and P_r represent dead polymer and polymer radicals respectively and k_d and k_t are the rate constants for depropagation and termination. The rate constant k_d includes all volatile products, e.g. dimer, trimer etc., evolved during the reation. I is the rate of initiation.

The rate of volatilisation = $k_d(P)$

But since in the steady state, $\frac{dP}{dt} = 0 = I - k_t(P)^2$

the rate of volatilisation = $k_d/k_t^{\frac{1}{2}} \times I^{\frac{1}{2}} = K.I^{\frac{1}{2}}$

It is assumed that at the point where weak link scission is complete, namely 27% volatilisation, the chain length of the depropagation reaction is identifiable with the chain length of the molecule at that point. Comparing Figs.14 and 16 for the degradation of S.5 at 280°C, the rate of volatilisation at this point is 1.5% per hour. Since each chain once activated disappears, it follows that:-

Rate of initiation = Rate of volatilisation = 1.5% per hour.

Where weak links break by a disproportionation mechanism the rate of initiation is proportional to the number of chain ends, and hence is inversely proportional to the molecular weight.

The average rate of initiation during the time that the molecular weight falls to half its original value, may be taken as the rate at a point midway between these extremes. The molecular weight at this point has fallen to 249,000 and hence the rate of initiation is proportional to 1/249,000 i.e. to 4×10^{-6}.

In the same way the rate of initiation at 27%

is proportional to 1/115,000 i.e. to 8.7×10^{-6}.

Thus the rate at the point defined above, relative to that at 27% volatilisation is $4/8.7 = 0.46$ and the rate of initiation must therefore be 1.5×0.46.

Therefore the rate of volatilisation = $(1.5 \times 0.46)^{\frac{1}{2}} = 0.83\%$ per hour.

If on the other hand weak link scission produces radicals then the rate of initiation will be given by the above value, 1.5×0.46, plus the average rate of initiation from radical chain ends. During the first ten hours of degradation, which includes the point being considered, on the average one weak link per molecule dissociates into radicals.

Hence the rate of initiation from radical chain ends in percent per hour $= \frac{115,000 \times 2 \times 100}{332,000 \times 10}$

and therefore the total rate of initiation

$$= (1.5 \times 0.46 + \frac{115,000 \times 2 \times 100}{332,000 \times 10})$$

$$= 7.6$$

As before, the rate of volatilisation = $7.6^{\frac{1}{2}} = 2.76\%$ per hour.

The theoretical rate of volatilisation can now be compared with the experimental rate obtainable from

Figs.14 and 16. Up to the point where on the average one bond is broken per molecule this is 0.75% per hour. This agrees more closely with the value derived above for chain scission by disproportionation showing weak link scission is not directly related to the production of volatile material.

Polymer degradation reactions carried out in the solid or viscous phase may be influenced to a considerable extent by the presence of a cage effect in which radicals produced by chain scission are unable to diffuse apart and consequently recombine.[45] The mechanism proposed above for the degradation of polystyrene is dependent upon disproportionation at radical chain ends following the homolytic fission of weak links in the polymer molecule. It is therefore not improbable that the overall rate of chain scission is governed by the relative rates of disproportionation, and recombination of radicals due to a cage effect. Provided, however, that the weak link structure is not destroyed during chain scission and recombination, the extent of the degradation will remain unaffected.

5. Summary of The Reaction Mechanism.

From the results discussed above it is suggested that degradation is initiated in polystyrene by chain

scission at a limited number of weak links which are distributed at random along the polymer molecule. The precise nature of the weak links is not specified, but a qualitative kinetic survey of the rate of volatilisation following chain scission would suggest that these structures break down by a disproportionation mechanism similar to that occurring in the termination of polymerising radicals. The presence of a labile group is therefore inferred. In the absence of conclusive evidence that oxygenated structures are responsible for weak link formation, this labile group may well be the tertiary hydrogen atom already present in the polymer chain. The chain scission reaction will result in the formation of double and single bond chain ends which subsequently degrade. The rate maximum in the volatilisation curves can therefore be explained on the basis of the increasing number of degradable chain ends produced by the chain scission reaction. Once degradation is initiated at the chain ends, the radicals produced split off monomer and higher chain fragments in a reverse polymerisation reaction, the chain length of which is of the order of 600.

This reaction scheme differs from that originally proposed by JELLINEK[11] in two respects. Firstly it has been shown that weak links do not disappear without chain

scission and secondly that the chain length of the reverse polymerisation reaction following chain scission is much longer than had hitherto been supposed.

The absence of intermolecular transfer has been inferred from the constancy of the ratio of non-monomeric to monomeric material observed throughout the course of the reaction, and the maximum rate in the volatilisation curves, previously attributed by SIMHA[21,44] to a random mechanism based on transfer, explained in terms of the weak link theory.

CHAPTER IV

THE POSSIBLE NATURE OF THE WEAK LINKS IN POLYSTYRENE

1. Introduction

The mechanism outlined in the previous chapter satisfactorily accounts for the various features of the degradation of polystyrene as observed by previous workers.[11,17] The rapid fall in molecular weight during the initial stages of the reaction has been attributed to chain scission at weak links which are regarded as being distributed at random along the polymer chain. The possible chemical nature of the weak links has not, however, been discussed.

It has hitherto been suggested, and generally accepted, that structures which are less stable thermally than the normal carbon-carbon bond in the polymer chain, are formed by the incorporation of oxygen into the polymer molecule either during or after polymerisation. Nevertheless it is also possible that abnormal structures produced during the polymerisation process itself, may be responsible for weak links formation. Structural irregularities formed as the result of the head to head

addition of monomer units or the formation of chain branches immediately suggest themselves as the most obvious sources of potential weak link structures.

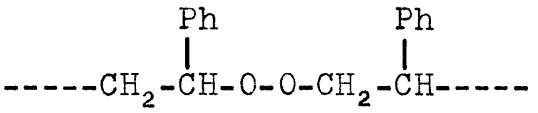
The principal difficulty in studying the thermal breakdown of polystyrene is that the concentration of weak links necessary to account for the decrease in molecular weight during degradation is so small that it is extremely doubtful whether they could be identified chemically, or even by using sensitive physical methods such as infra-red spectrascopy. The formation of weak links will, however, be determined by the conditions of polymerisation, and by relating any change in the proportion of weak links present to the corresponding variation in the polymerising system, it should be possible to deduce a certain amount about the nature of the weak link.

The effect of altering a number of polymerisation variables on the concentration of weak links in polystyrene will therefore now be discussed.

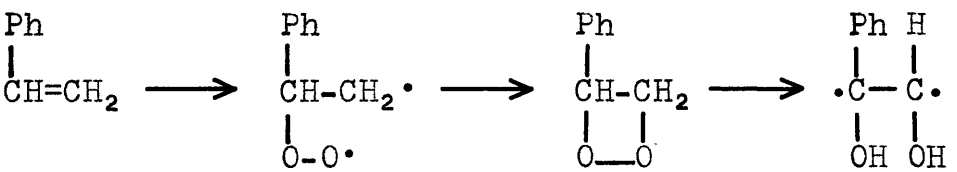
2. Oxygenated Structures as a Source of Weak Links.

STAUDINGER[4] and JELLINEK[11] have both suggested that chain scission in the degradation of polystyrene occurs at oxygenated structures which are formed by the interaction of the polymer with oxygen during the polymerisation process. While Staudinger favours the copolymerisation of oxygen into

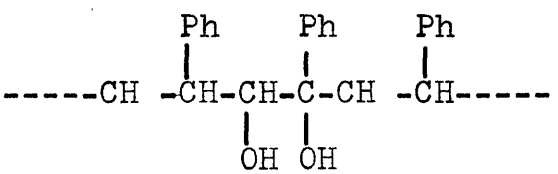
the polymer chain -



Jellinek suggests that oxygen reacts with the monomer during polymerisation to form a 1:2-glycol type bi-radical -

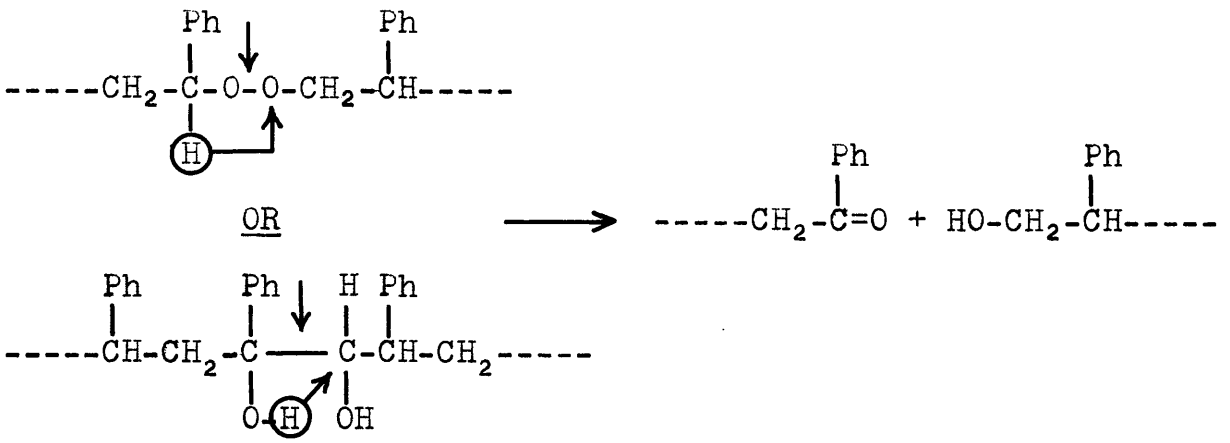


which is incorporated into the polymer chain -



Either of these reactions may be responsible for the formation of weak links.

The rapid fall in molecular weight during degradation may then be associated with a chain scission reaction proceeding in the following way -



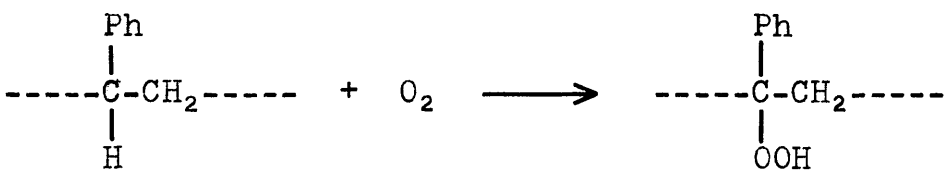
which is followed by further degradation from the chain ends with the resultant production of monomer and other volatile products.

The initial step in attempting to determine the weak link structure must obviously be to assess the probable importance of such reactions.

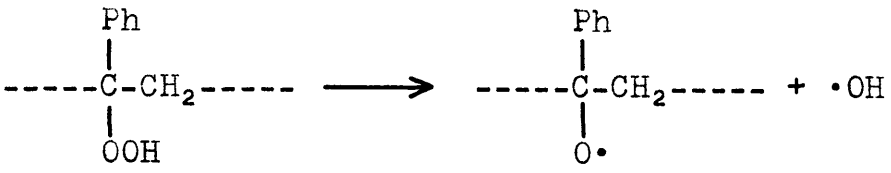
The careful purification of both catalyst and monomer by the methods indicated in Chapter II, followed by the thorough degassing of the monomer before distillation under vacuum into the dilatometers, should ensure the complete removal of oxygen and other impurities from the polymerisation system. The complete exclusion of oxygen from the polymerisation can finally be ensured by sealing off the dilatometers under vacuum. The fact that polymers S.3, 4 and 5, which were prepared under such conditions,

still exhibit a large decrease in molecular weight on degradation, suggests that oxygen is not responsible for weak link formation. Indeed there is no significant difference in the degradation properties of polymers prepared in air and in vacuo but under otherwise identical conditions.[11,46]

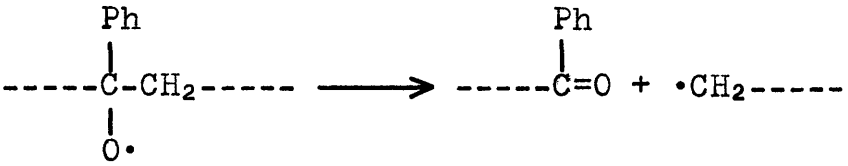
Weak link structures may, however, still be produced by oxidation of the polymer during storage. It is known, for example, that prolonged exposure of polystyrene films to light and air results in the appearance of bands at 3450 cm^{-1} and 1730 cm^{-1} in the infra-red spectrum of the polymer. These ACHHAMMER[25] attributes to hydroxyl and carbonyl groups respectively, presumably produced by the decomposition of hydroperoxide groups, formed during the oxidation of the polymer:-



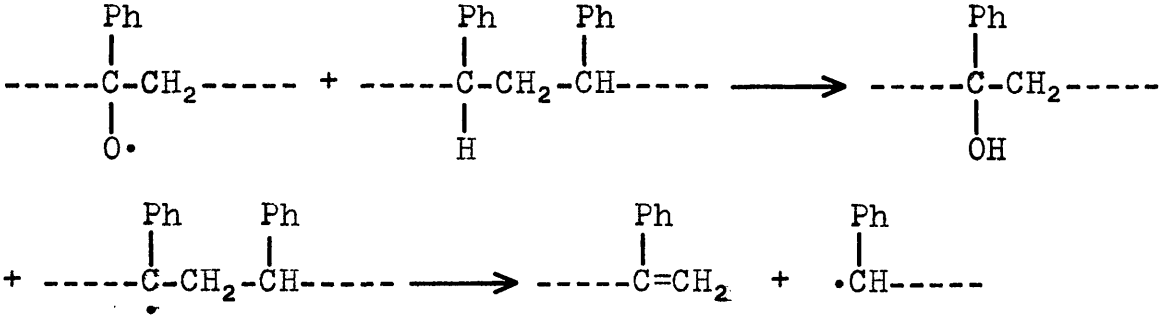
Decomposition of hydroperoxide groups at elevated temperatures would almost certainly result ultimately in chain scission -



followed by -



or,



and such structures must accordingly be considered as another possible source of weak links.

Previous results show that the rate of oxidation at room temperature is comparatively slow.[25] Nevertheless, if such a reaction does occur, the number of weak links present will increase with the time of storage and the extent of degradation should change accordingly. Results for the degradation of polymer S.4 at 298°C as observed one month

POLYMER S4.

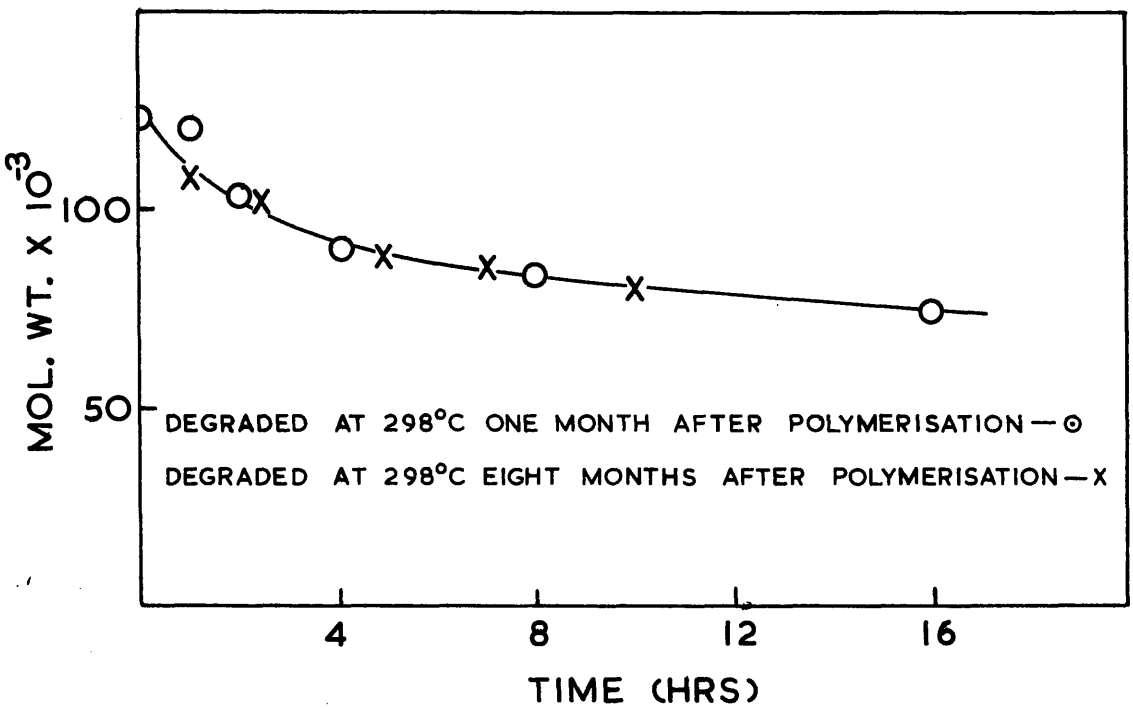


FIG. 20.

and eight months after polymerisation are given in Table VII and plotted in Fig.20.

TABLE VII

Degradation of Polymer S.4 at 298°C.

One month after preparation.		Eight months after preparation.	
Time (Hrs.)	Mol. Wt.	Time (Hrs.)	Mol. Wt.
1.0	120,300	1.0	108,000
2.0	104,400	2.5	103,500
4.0	90,010	5.0	89,910
8.0	84,220	7.0	87,120
16.0	74,300	10.0	80,720

Agreement between the two sets of results is excellent, and it is therefore impossible to account for the rapid fall in molecular weight observed after storage for one month in terms of oxidation of any of the normal structures in the polymer.

These results show that the incorporation of oxygen into the polymer molecule either during or after polymerisation is not responsible for weak link formation in the polymers examined.

3. Other Possible Weak Link Structures.

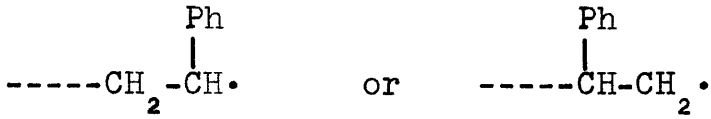
Since the weak links normally present in polystyrene are not oxygenated structures it must be presumed

that they are formed during the polymerisation process itself in some abnormal reaction step. It is therefore convenient at this point to consider how abnormal structures may arise during polymerisation and how the proportion of such structures should vary with the polymerisation conditions. If polymers subsequently prepared in accordance with these theoretical predictions, degrade in the expected manner it may be assumed that the source of weak links has been identified.

(i) The Head to Head Addition of Monomer Units.

One of the most probable sources of weak links is the head to head addition of monomer units.

The structure of the radical chain end in the polymerisation of styrene must either be -

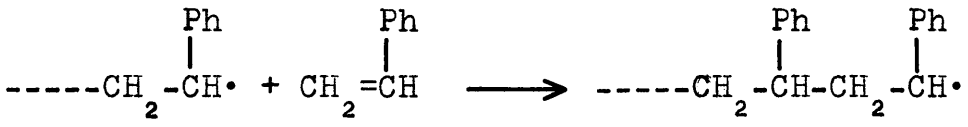


I II

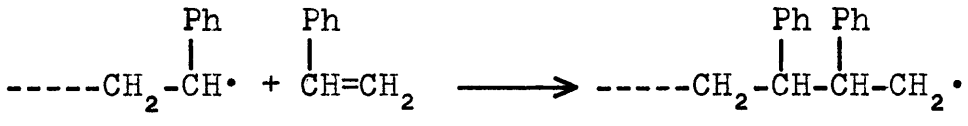
Since the head to head addition of monomer units can only take place by the addition of monomer to radical I it will be convenient to consider this structure alone.

The addition of monomer to this radical during polymerisation can take place either by head to tail

addition,

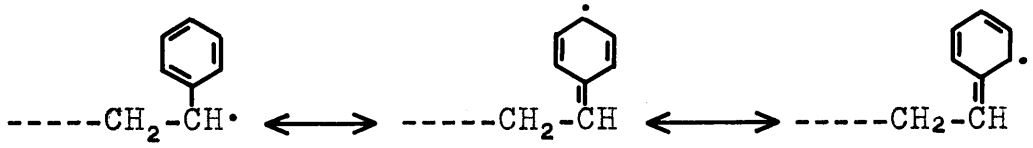


or by head to head addition,



the relative rates of these two processes depending on the stability of the radicals produced. Head to tail addition reproduces the radical structure I, while head to head addition results in the production of structure II.

Radical I is resonance stabilised by the presence of the benzene ring on the carbon atom carrying the odd electron -



In structure II, however, the benzene ring is situated on the β-carbon atom and is therefore unavailable for the formation of resonance structures. Radical I is therefore more stable than radical II and its formation is accordingly more probable.

FLORY[47] points out that a comparison of the

carbon-iodine bond strengths in methyl iodide and benzyl iodide and a similar comparision of the carbon-hydrogen bond strengths in methane and toluene, indicates that a benzyl radical of type I is favoured by resonance stabilisation to the extent of 20 to 25 k.cals. Radical II which is a β-phenylethyl analog will not differ greatly in stability for an ethyl or methyl radical and hence the formation of radical I should be favoured over the formation of radical II by an energy difference of about the same amount. Although resonance stabilisation in the transition state is substantially less than the resonance energy of the product, the activation energy for head to tail addition should, nevertheless, be lower than that for head to head addition by about 8 to 10 k.cals.

A slightly lower energy of activation for the head to tail process might also be predicted from steric considerations since the bulky nature of the phenyl group would not favour head to head addition.

If k_{HT} and k_{HH} are the rate constants for head to tail and head to head addition respectively, and if k_{HH} is small compared to k_{HT}, then -

$$\frac{\text{The rate of head to tail addition}}{\text{The rate of head to head addition}} = Q = \frac{k_{HT}(P)(M)}{k_{HH}(P)(M)}$$

$$= \frac{A_{HT} \cdot e^{-E_{HT}/RT}}{A_{HH} \cdot e^{-E_{HH}/RT}}$$

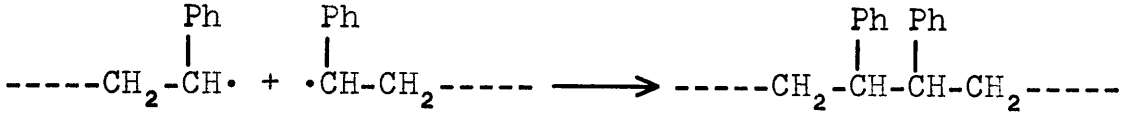
where (M) represents the concentration of monomer and (P) the concentration of growing polymer radicals. E is the energy of activation and A the temperature independent factor for each process as indicated by the subscript. R is the Gas Constant and T the temperature of polymerisation. Since the energy of activation for head to head addition would be expected to be higher than that for head to tail addition, $\Delta E = (E_{HH} - E_{HT})$ will be positive, and therefore putting $\Delta E = (E_{HH} - E_{HT})$ and $A = A_{HT}/A_{HH}$ the above expression simplifies to -

$$Q = A \cdot e^{\Delta E/RT}$$

It follows that Q varies inversely as the temperature of polymerisation and therefore that the rate of head to head addition increases relatively faster than the rate of head to tail addition as the temperature is raised.

The bulk of experimental evidence reported to date suggests that termination in the polymerisation of

styrene takes place by the combination of radicals [27,28,29] -



a reaction which will result in the production of a head to head linkage in the polymer chain. This means that if head to head linkages are responsible for weak link formation, each molecule, irrespective of the molecular weight and temperature of polymerisation, contains a minimum of one weak link. From the results presented in Chapter III it was suggested that chain scission involved disproportionation rather than the production of free radicals. The number average molecular weight during the weak link scission phase of the degradation would therefore be expected to fall to at least half its original value.

Thus if the head to head addition of monomer units is responsible for weak link formation and if previous workers are correct in deducing that termination occurs exclusively by the combination of radicals, it can be predicted that the number of weak links will increase as the temperature of polymerisation is raised and that the number of weak links present per molecule cannot be less than one.

(ii) Chain Branching

The presence of chain branches may provide yet another possible source of weak links. Although BEVINGTON, GOZMAN and MELVILLE[30], and BROWN and WALL[31] have reported the extent of branching during the polymerisation of styrene to be negligible, it was nevertheless considered important to investigate this aspect of the polymerisation process, since the number of branches necessary to account for the observed decrease in molecular weight during degradation would be extremely small.

Branching during polymerisation proceeds through transfer to polymer, and has a slightly higher energy of activation (7 k.cals./mole)[30] than the competing propagation reaction (6.3 k.cals./mole).[46] Consequently branching would be favoured at higher temperatures of polymerisation.

The degree of branching will obviously also increase with the extent of conversion of monomer to polymer since the probability of transfer must depend on the amount of polymer present in the system. The relative rates of branching and propagation in any polymerising system may be obtained in the following way[49]:-

Let α be the number of monomer molecules which have polymerised out of a total of N in the system, and Υ be the total number of branches. (P) represents the

concentration of polymer radicals.

The rate of polymerisation will be given by-

$$\frac{d\alpha}{dt} = k_p(P)(1-\alpha)$$

and the rate of production of chain branches by -

$$\frac{d\Upsilon}{dt} = k_{tr}(P).\alpha N$$

where k_p and k_{tr} are the rate constants for propagation and transfer to polymer respectively.

Hence,

$$\frac{d\Upsilon}{d\alpha} = \frac{k_{tr}.\alpha N}{k_p(1-\alpha)}$$

Integrating from 0 to α with $\Upsilon = 0$ at $\alpha = 0$ -

$$\frac{\Upsilon}{\alpha N} = -\frac{k_{tr}}{k_p}\left[1 + \frac{1}{\alpha}\ln(1-\alpha)\right]$$

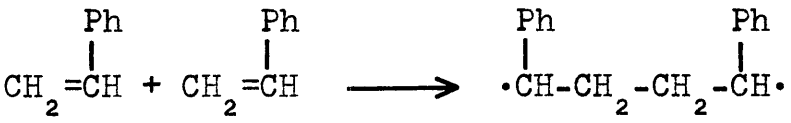
The relative amount of branching must therefore increase rapidly with conversion irrespective of the absolute magnitude of the transfer constant for branching.

If weak links are due to chain branching the number of weak links present in the system should therefore increase with temperature for polymers polymerised to the same extent, and also with conversion for polymers prepared at the same temperature.

(iii) The Nature of The Chain Ends in Polystyrene -

Since termination in the polymerisation of polystyrene occurs by the combination of radicals, the nature of the chain ends will be determined solely by the method of initiation. Thus in benzoyl peroxide initiated polymerisation catalyst fragments will be present at both ends of the polymer chain.

The nature of the initiation process in the absence of catalyst has not yet been unambiguously established. FLORY[50] has suggested that diradical initiation -



is energetically more probable than the possible hydrogen transfer reaction -

a view which is supported by the reported isolation of a compound, during the initial stages of the benzoquinane inhibited polymerisation of styrene, whose formula corresponds to two molecules of styrene and one of benzoquinane.[51] The difficulty of reconciling diradical

initiation with termination by the combination of radicals is immediately obvious. ROSSELL and TOBOLSKY[52] have, however, suggested that a growing diradical will readily cyclise and that only those diradicals which are converted into monoradicals before cyclisation can take place, will give rise to high polymers. Termination in the resultant monoradical polymerisation would doubtless proceed in the normal manner and the chain ends in such polymers will thus be structural variants of the monomer unit. Variations in stability between these and chain ends formed by catalyst fragments might affect the degradation reaction.

The importance of chain ends in the degradation of polymethyl methacrylate has been clearly established by GRASSIE, MELVILLE and VANCE.[10,53] The stability of this polymer is closely dependent on the nature of the terminal structures in the polymer chain. The depolymerisation mechanism of polymethyl methacrylate differs, however, from that of polystyrene, in that degradation occurs solely from the chain ends. It is therefore difficult to see how the nature of the chain ends in polystyrene can affect the degradation which is apparently governed by a chain scission mechanism. Nevertheless it would be unwise to neglect this possibility which can readily be investigated by preparing polymers in the presence and absence of catalyst and by

initiating the polymerisations both photochemically and thermally.

(iv) The Molecular Weight of the Undegraded Polymer

The possible influence of the molecular weight of the undegraded polymer on the degradation must also be investigated.

One of the features of both the ultrasonic and mechanical degradation of polystyrene is that, irrespective of the molecular weight of the undegraded material, degradation appears to come to a standstill at a molecular weight of approximately 100,000.[54,55] In the case of mechanical degradation much discussion has centred round the question of whether or not the mechanical energy has first to be dissipated into heat before degradation results. If such an energy conversion occurs then degradation is thermal rather than mechanical.

The fact that degradation of polystyrene under the influence of mechanical forces ceases at approximately the same molecular weight for all polymers, can be explained in the following way.

It is reasonable to suppose that up to a certain chain length polymer molecules will be capable of yielding to mechanical stress because of the flexibility of the long

chain molecule. As the molecular weight rises, the inertia of the molecule will increase until a certain chain length is reached at which the polymer molecule will no longer be able to yield to the mechanical forces acting on it, and chain rupture will occur. Degradation will then continue until the polymer chains are again sufficiently small to yield to the applied forces. As it is not altogether improbable that an exactly similar reaction may occur by virtue of the thermal motion of the polymer chains at elevated temperatures, the importance of examining the extent of degradation in relation to the molecular weight of the undegraded polymer should not be overlooked.

4. Interpretation of Results - Estimation of the Number of Weak Links Present.

The degradation of polystyrene involves two separate reactions which proceed simultaneously, namely chain scission and reverse polymerisation from the chain ends.

The number of weak links per molecule, s, originally present in the polymer chain, is given by the formula:-

$$s = \frac{Mo}{M_d} - 1$$

in which M_o is the number average molecular weight of the

undegraded polymer and M_d is the limiting value to which the molecular weight of the polymer would fall as a result of chain scission in the complete absence of depropagation.

The fall in molecular weight up to 30% volatilisation is due predominantly to chain scission, but the molecular weight at this point does not accurately represent M_d since superimposed on this fall will be a small component decrease in molecular weight due to the reverse polymerisation process. Complete mathematical analysis of the molecular weight-conversion curves in terms of these two reactions would be extremely complicated and scarcely warranted by the accuracy of the experimental points.

It has already been pointed out in Chapter III that the slope of the molecular weight-conversion curve for extents of degradation greater than 30% shows that the chain length of the reverse polymerisation reaction is of the order of the chain length of the polymer molecule after weak link scission is complete. Had the chain length of this reaction been greater than the chain length of the degraded molecule, the curve of molecular weight versus percentage volatilisation above 30% conversion would have been parallel to the volatilisation axis, and M_d would have been directly obtainable. The experimental curves, however, show that during this phase of the reaction the molecular weight

continues to fall slowly in a more or less linear manner and the slope of this part of the curve gives the rate of decrease in molecular weight due to the reverse polymerisation process. An approximate estimate of the contribution of this reaction to the fall in molecular weight up to 30% conversion, can therefore be obtained by extrapolating the linear portion of the molecular weight-conversion curves back to zero extent of volatilisation. The molecular weight at this point will represent approximately the limit to which the molecular weight of the polymer would fall as a result of chain scission at weak links in the complete absence of depolymerisation from the chain ends, and will be taken to represent M_d in the above formula.

As the number of weak links present in polymers of different molecular weights will have to be compared, it is more convenient to discuss the results in terms of the number of weak links present per monomer unit, S. This is independent of the molecular weight of the polymer and is given by -

$$S = \frac{s \times 10^4}{M_o} \quad \text{or directly by} \quad S = 10^4\left[\frac{1}{M_d} - \frac{1}{M_o}\right]$$

10^4 being the molecular weight of styrene monomer.

5. Results.

The degradation characteristics of seven polymers prepared within the temperature range 30° to 120°C were examined. Details of the preparation of these polymers are given in Table VIII below. It can be seen that the preparation of the polymers has been designed to allow discussion of the effect on the degradation of all the possible structural variations mentioned in section 3 above.

TABLE VIII

Details of the preparation of polymers S.3 to S.11

Polymer	Temp. of Polymer-isation	Method of Initiation	Catalyst Percent Wt./Vol.	Extent of Polymer-isation	Mol. Wt. M_o
S.8	30°C	U.V. light	1.00	15	99,080
S.11	30°C	U.V. light	0.30	15	130,200
S.4	60°C	Thermal	Approx. 0.30	15	122,700
S.5	60°C	Thermal	Approx. 0.30	5	332,400
S.3	90°C	Thermal	None	15	Approx. 10×10^6
S.6	90°C	Thermal	0.03	15	315,800
S.7	120°C	Thermal	None	15	421,000

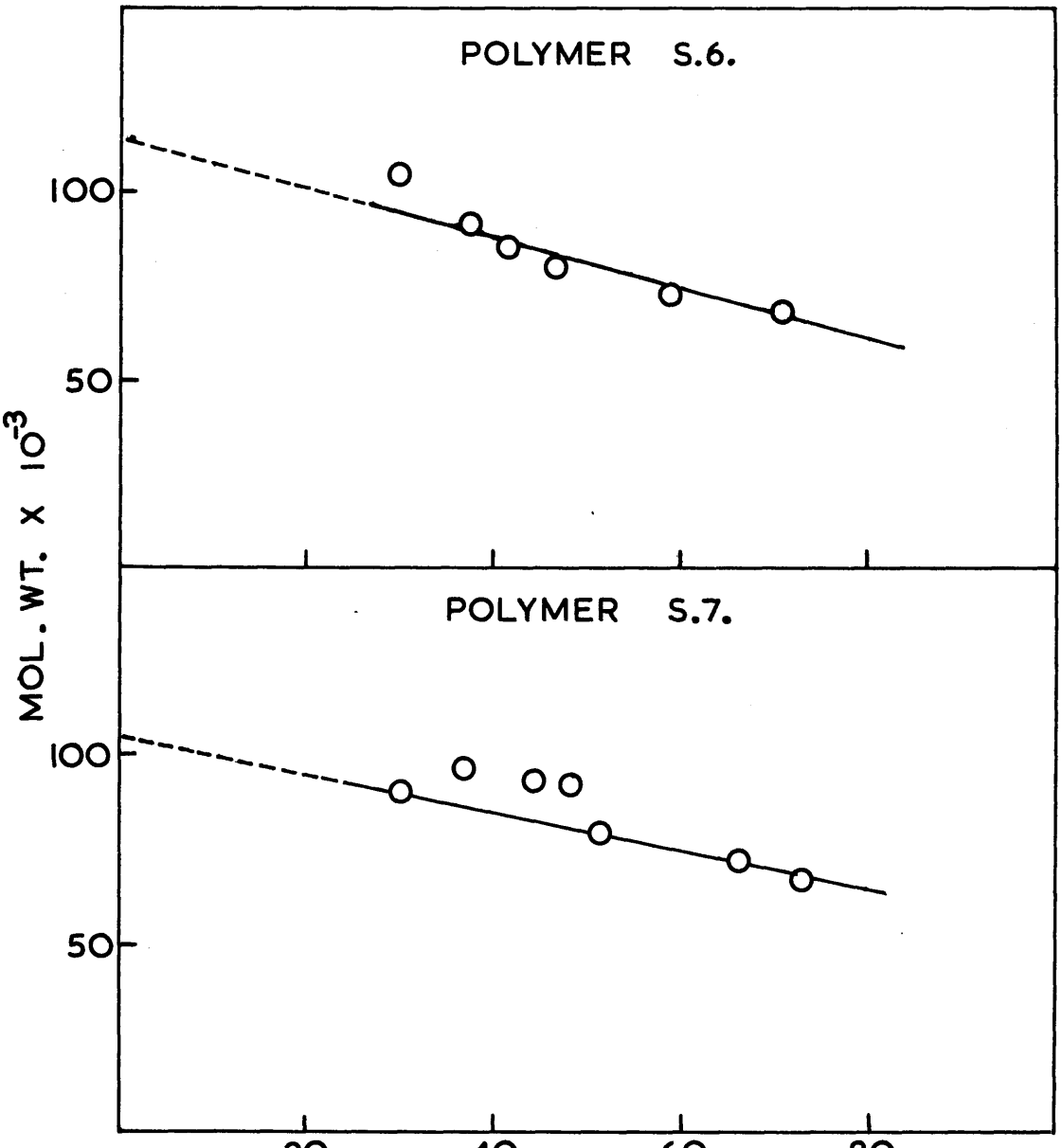

POLYMER S.6.
POLYMER S.7.
100
50
100
50
MOL. WT. X 10^{-3}
20
40
60
80
% VOLATILISATION

FIG. 21.

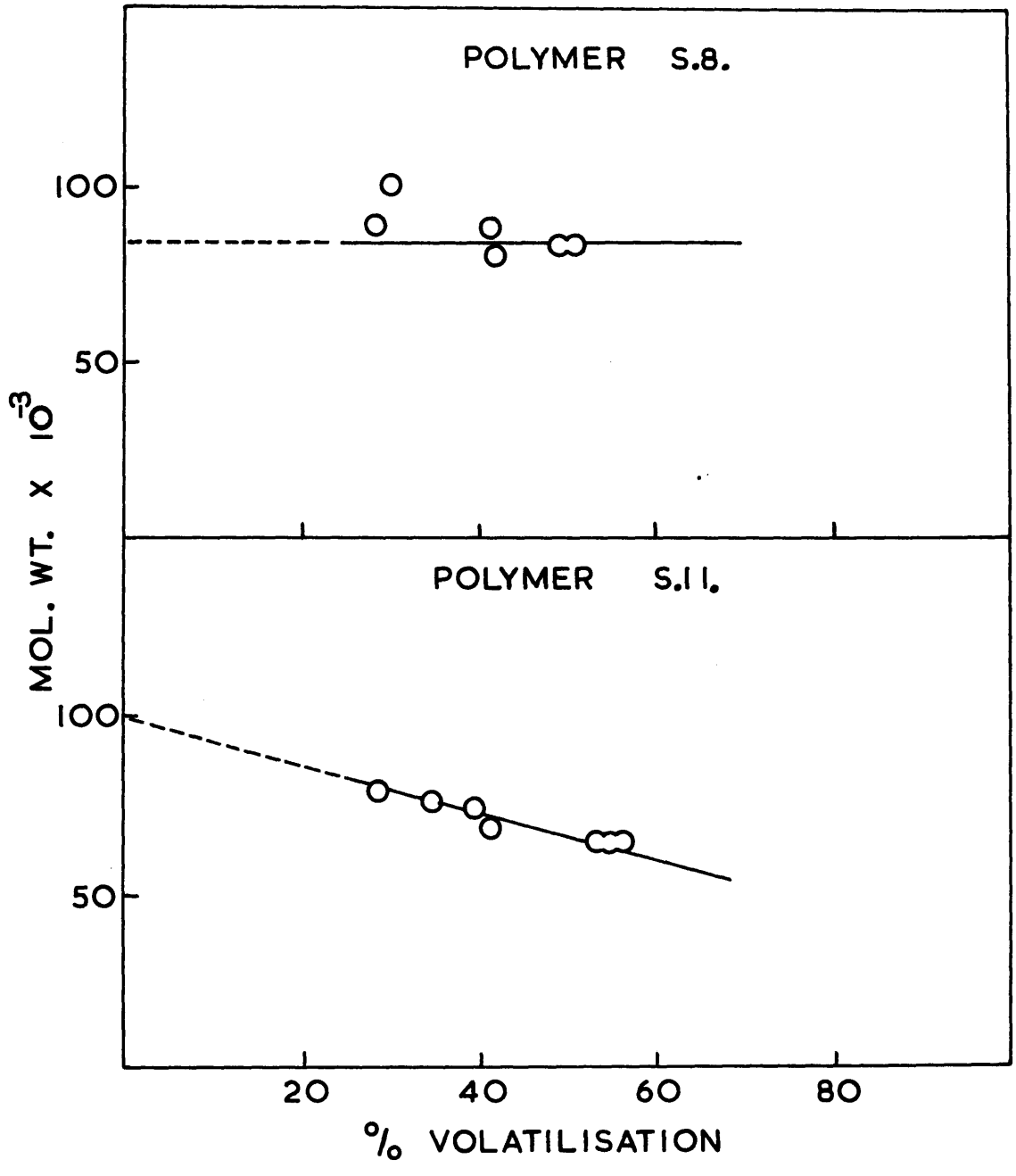

POLYMER S.8.
100
50
POLYMER S.11.
100
50
MOL. WT. x 10^{-3}
20
40
60
80
% VOLATILISATION

FIG. 22.

The molecular weight-conversion data for the degradation of polymers S.6,7,8 and 11 at 290°C, is given in Table IX and Figs. 21 and 22. The corresponding data for polymers S.3,4 and 5 has already been given in Chapter III.

TABLE IX

Molecular weight-conversion data for the degradation of polymers S.6,7,8 and 11 at 290°C.

Polymer S.6

Molecular Weight - 315,800

Mol. Wt.	% Volatilisation
105,300	30.02
92,190	37.84
85,650	41.71
80,210	46.86
73,650	59.02
68,280	71.29

Polymer S.7

Molecular Weight - 421,000

Mol. Wt.	% Volatilisation
90,220	30.68
90,220	30.70
97,160	36.85
93,560	44.67
92,190	48.58
79,950	51.40
72,180	66.21
67,540	73.05

Polymer S.8

Molecular Weight - 99,080

Mol. Wt.	% Volatilisation
89,280	28.44
100,200	30.11
87,720	41.72

Polymer S.11

Molecular Weight - 130,200

Mol. Wt.	% Volatilisation
78,960	28.40
76,560	34.62
74,300	39.56

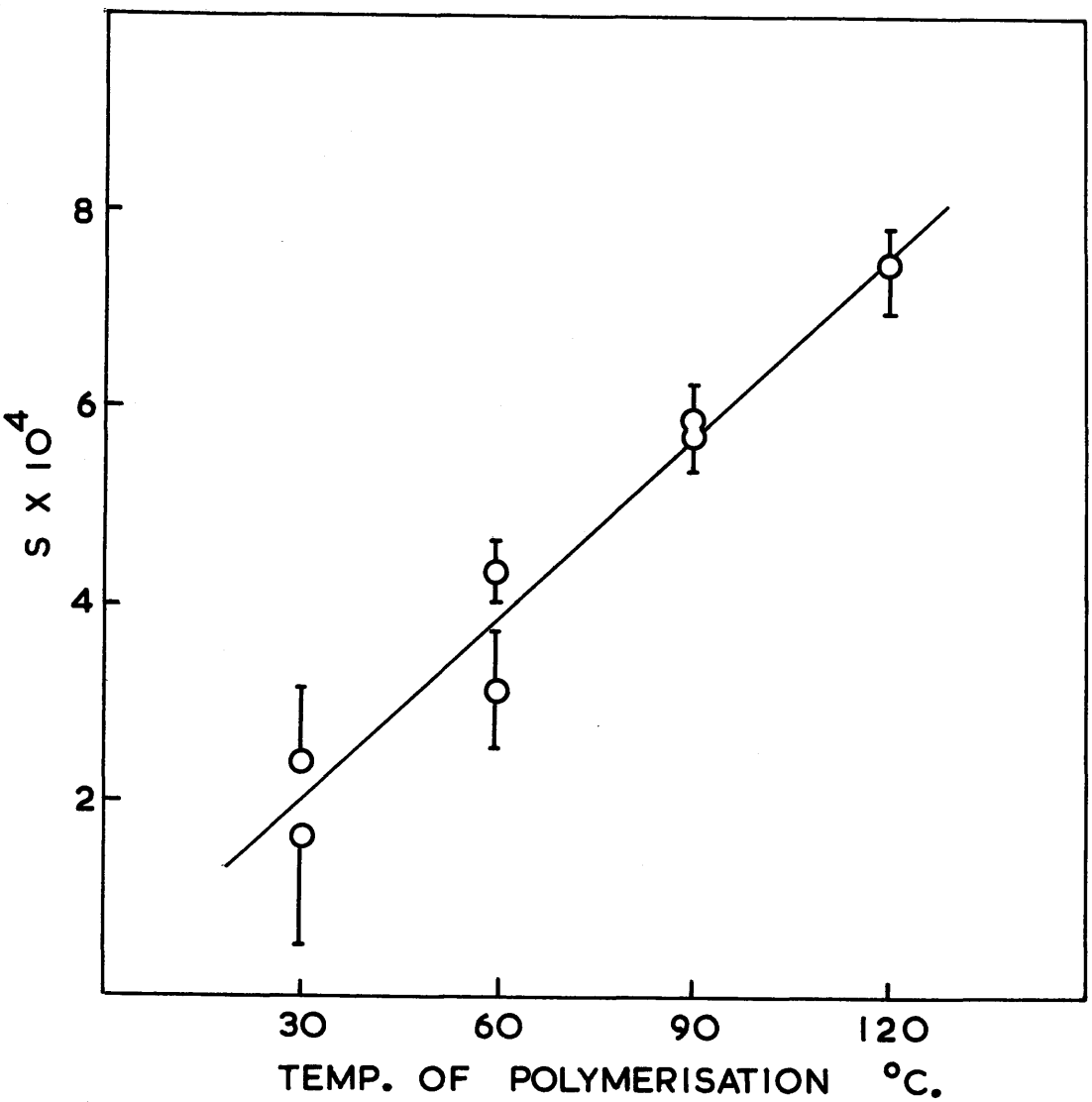


FIG. 23.

TABLE IX (Cont.)

Polymer S.8		Polymer S.11	
Mol. Wt.	% Volatilisation	Mol. Wt.	% Volatilisation
80,460	42.19	68,870	41.22
83,100	49.84	64,770	53.52
83,100	51.34	64,770	54.84
		64,770	55.56

For each of these polymers the value of M_d was obtained by extrapolation as described above, and the number of weak links per molecule, s, and per monomer unit, S, calculated. The summarised degradation data is presented in Table X. Preliminary inspection reveals an upward trend in S as the temperature of polymerisation is raised. This is illustrated in Fig. 23.

TABLE X

Summarised data for the degradation of polymers at 290°C.

Polymer	Temp. of Polymer-isation	M_o	M_d	s	S
S.8	30°C	99,080	85,000	0.165	1.60×10^{-4}
S.11	30°C	130,200	100,000	0.302	2.41×10^{-4}
S.4	60°C	122,700	90,000	0.363	3.08×10^{-4}
S.5	60°C	332,400	140,000	1.375	4.29×10^{-4}

TABLE X (Cont.)

Polymer	Temp. of Polymer-isation	M_o	M_d	s	S
S.6	90°C	315,800	115,000	1.746	5.75×10^{-4}
S.3	90°C	Approx. 10×10^6	180,000	54.55	5.67×10^{-4}
S.7	120°C	421,000	105,000	3.01	7.44×10^{-4}

The value of S will depend closely on the accuracy of the extrapolation of the molecular weight-conversion curves, particularly where the molecular weight of the undegraded polymer is relatively low and only a small decrease in molecular weight occurs during degradation, e.g. in polymers S.4, 8 and 11. The estimated error in the calculation values quoted in Table X is indicated by the vertical line drawn through the points plotted in Fig. 23.

6. Discussion of Results

It will be convenient in analysing the above results to consider them independently in relation to each of the possible sources of weak links already mentioned, (See section 3). Before discussing these results, however, it must be pointed out that the object of these experiments

was to make a preliminary survey of the problem and to determine in a qualitative fashion the possible source of weak link formation. Any conclusions reached below must therefore await the results of a more detailed investigation before it can be said that the problem has been finally resolved.

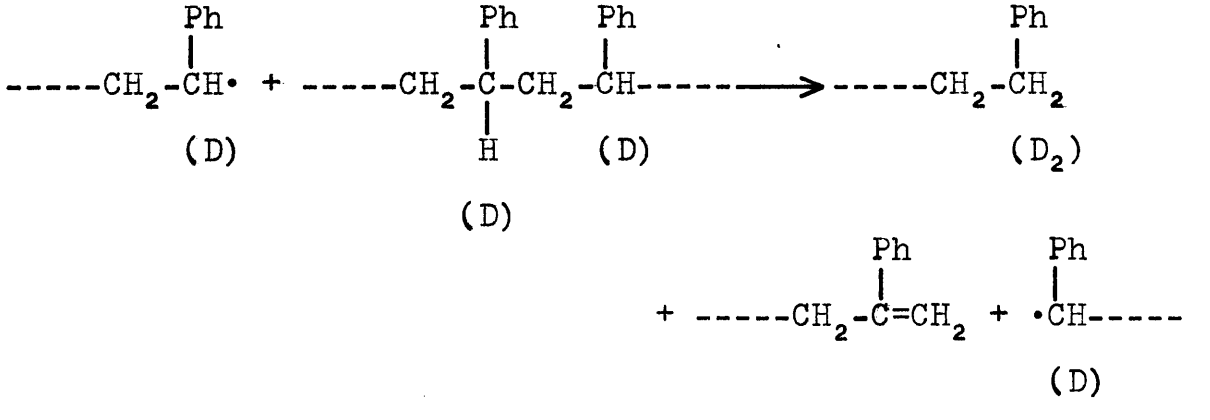
(1) The Head to Head Addition of Monomer Units -

In discussing the head to head addition of monomer units as a possible source of weak links, it was pointed out above that the number of such structures present should increase as the temperature of polymerisation is raised. This is in agreement with the observed increase in S for the polymers examined.

Consideration of the number of bonds broken per molecule, however, reveals that for polymers S.4, 8 and 11 the experimental value of s is less than one, and that on the average less than one molecule in three has undergone chain scission. Since termination in the polymerisation of styrene takes place by the combination of radicals, each molecule must contain at least one head to head structure or weak link. The low values of s observed cannot therefore be explained. It is also difficult on the basis of this weak link structure to account for the difference in the rates of

degradation of polystyrene and poly-α-deuterostyrene reported by WALL and his coworkers.[23]

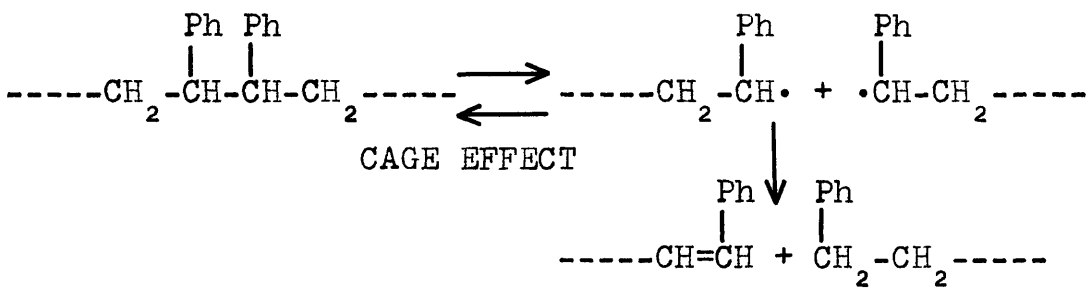
Wall has suggested that if weak links are responsible for the fall in molecular weight during the degradation of polystyrene, then the rates of degradation of polystyrene and poly-α-deuterostyrene should be the same. If, on the other hand, degradation occurs by intermolecular transfer -



then the rate of degradation of poly-α-deuterostyrene should be lower than that of polystyrene since the rate of abstraction of a tertiary deuterium atom would be expected to be slower than that for a tertiary hydrogen atom. On examining both reactions, Wall found that the rate of chain scission of poly-α-deuterostyrene was only about half that of polystyrene, which would appear to confirm the above theory. If, however, the lower rate of degradation of poly-α-deuterostyrene could be explained in terms of a weak

link structure, the final ambiguity in the results reported by previous workers would have been resolved.

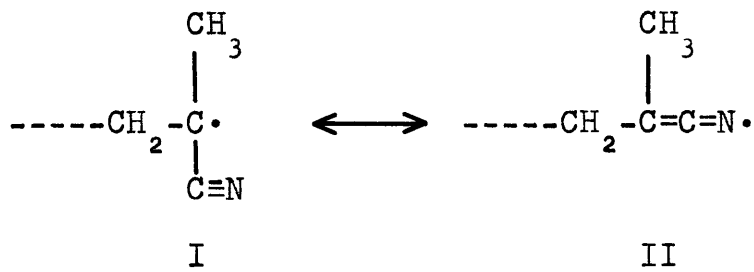
The experimental results reported in Chapter III suggest that chain scission occurs by disproportionation rather than by the formation of radicals which immediately split off monomer. Assuming the weak link to be formed by the head to head addition of monomer units, chain scission would most probably take place in the following way -



and the overall rate of chain scission is clearly dependent upon the abstraction of the β-hydrogen atom by the benzyl radical. If, on the other hand, disproportionation had involved abstraction of the α-hydrogen atom, which is not possible in terms of the weak link structure here considered, the lower rate of degradation of poly-α-deuterostyrene could be accounted for.

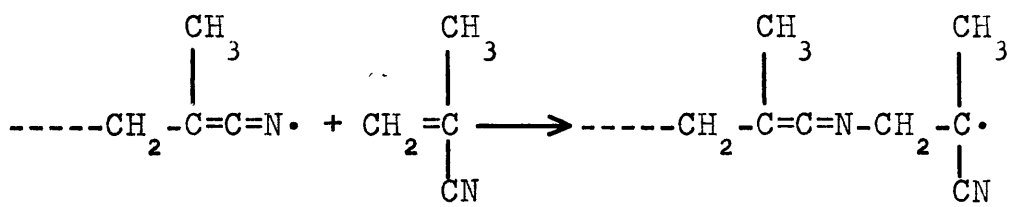
TALAT-ERBEN and BYWATER[56] have recently demonstrated the presence of ketene-imine linkages in polymethacrylonitrile. The polymerising radicals in this

system is resonance stabilised -

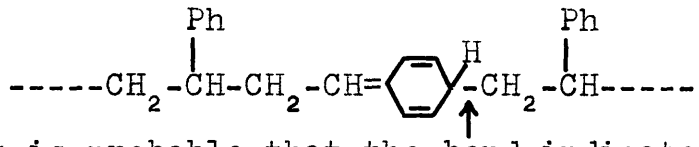


I II

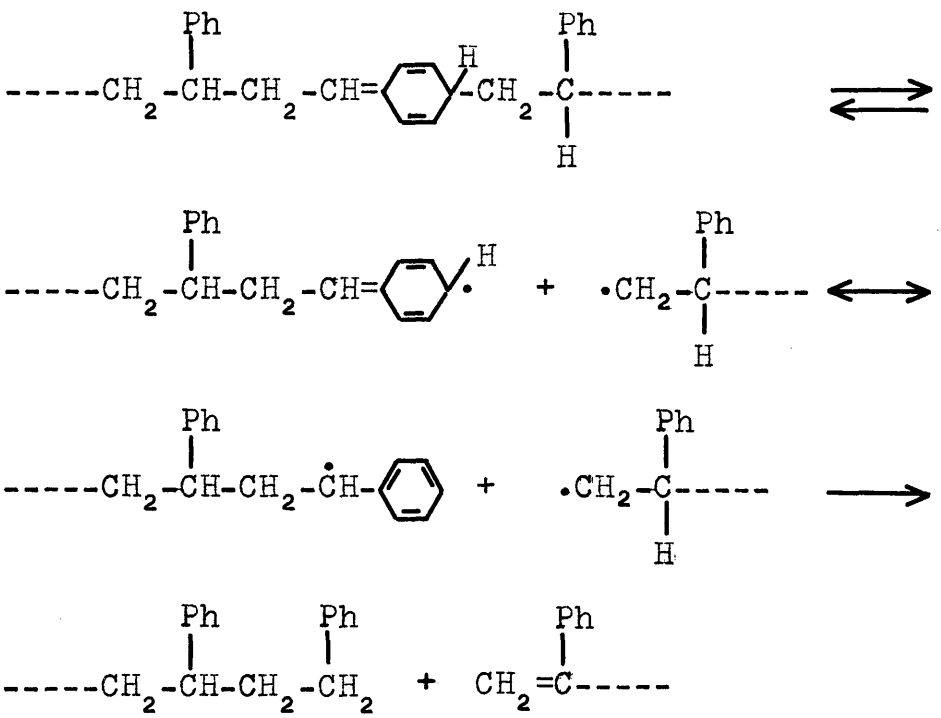
and they have suggested that ketene-imine linkages are formed when the radical II enters into polymerisation -



This has been confirmed by GRASSIE and McNEILL[57] who have shown that the occurence of these structures is dependent on the conditions of polymerisation. A similar reaction could also occur during the polymerisation of styrene, where the polymerising radical is again resonance stabilised. Here the reaction may be propagated through the ortho and para positions of the benzene nucleus. Addition in the ortho position is unlikely because of the possible shielding of the radical by the polymer chain and also from steric considerations. The para position would therefore present the most probable site for reaction. Addition in this position would result in the incorporation of the benzene ring into the polymer chain -



and it is probable that the bond indicated will be potentially weaker than the normal carbon-carbon in the chain since it is in the α-position to both double bonds of the quinoid ring system.[3] Chain scission at this point would probably be followed by revision of the ring system to the more stable benzenoid form, disproportionation following to stabilise the radicals produced:-



Disproportionation in this instance involves the transfer of the α-hydrogen atom and therefore offers a possible explanation of the lower rate of chain scission of poly-α-deuterostyrene. It is not, however, immediately obvious

from energy considerations why the abnormal mode of addition suggested here should be more favoured at higher temperatures.

(ii) Chain Branches -

Since the energy of activation for chain branching is slightly higher than that for propagation an increase in S with the temperature of polymerisation would be predicted and this is again in accord with the abserved effect.

BEVINGTON, GOZMAN and MELVILLE[30], using radio active tracer techniques, have shown, however, that the extent of chain branching during the polymerisation of styrene is negligible. They estimate that up to 75% polymerisation at 164°C, less than one molecule in ten is branched in a polymer of average molecular weight 78,000. This means that the frequency of chain branching up to this conversion, expressed in terms of the number of branches per monomer unit, must be something less than 1.3×10^{-4}. At the low conversions used in the present investigation, 5 and 15% polymerisation, the extent of branching must be considerably lower than this and it is therefore more than probable that the polymer molecules are almost exclusively linear. Consequently the rapid fall in molecular weight observed during the degradation of polymers prepared within

the temperature range 30° to 120°C is unlikely to be associated with the formation of weak links due to chain branching. This is further emphasised by consideration of the results for polymers S.4 and 5.

If it is assumed that chain branching occurs then from the theoretical treatment already given -

$$\frac{\text{The rate of chain branching}}{\text{The rate of polymerisation}} = \frac{k_{tr}.\alpha N}{k_p(1-\alpha)} = K\left(\frac{\alpha.N}{1-\alpha}\right)$$

which leads to the expression -

$$\frac{\Upsilon}{\alpha N} = -K\left[1 + \frac{1}{\alpha}\ln(1-\alpha)\right]$$

where α is the fraction of monomer molecules which have polymerised out of a total of N in the system, and Υ is the total number of branches. k_{tr} and k_p are the rate constants for chain branching and propagation respectively.

The left hand side of this equation gives the total number of branches present per monomer unit and is equivalent to S. By substituting the extents of conversion for polymers S.4 and S.5 it should be possible from this equation to derive the expected ratio of chain branching in these two polymers. When this is done it is found that the number of chain branches (or weak links) in S.4 to the number in S.5 should be in the ratio of 3:1. The experimental

ratio of 3.08:4.29 does not satisfy this theory.

Weak links cannot therefore be due to chain branching.

(iii) Chain Ends

If the chain ends in the depolymerisation of polystyrene in any way influence the chain scission reaction they must do so by presumably undergoing degradation to free radicals which are then capable of attacking the polymer chain in a manner similar to intermolecular transfer. Only under such conditions can the stability of the terminal structure in the polymer chain affect the chain scission process.

That the nature of the chain ends does not affect the extent of the chain scission reaction during the degradation of polystyrene is evident from the identical values of S observed for polymers S.3 and S.6. Reference to Table VIII shows that, with the exception of the method of initiation, these polymers were prepared under exactly identical conditions. Since previous discussion, (see page 73), has shown that the method of initiation is the only factor which determines the chain end structure, it must therefore be presumed that chain scission proceeds by a mechanism which is independent of any variation in the stability of the terminal structure in the polymer chain.

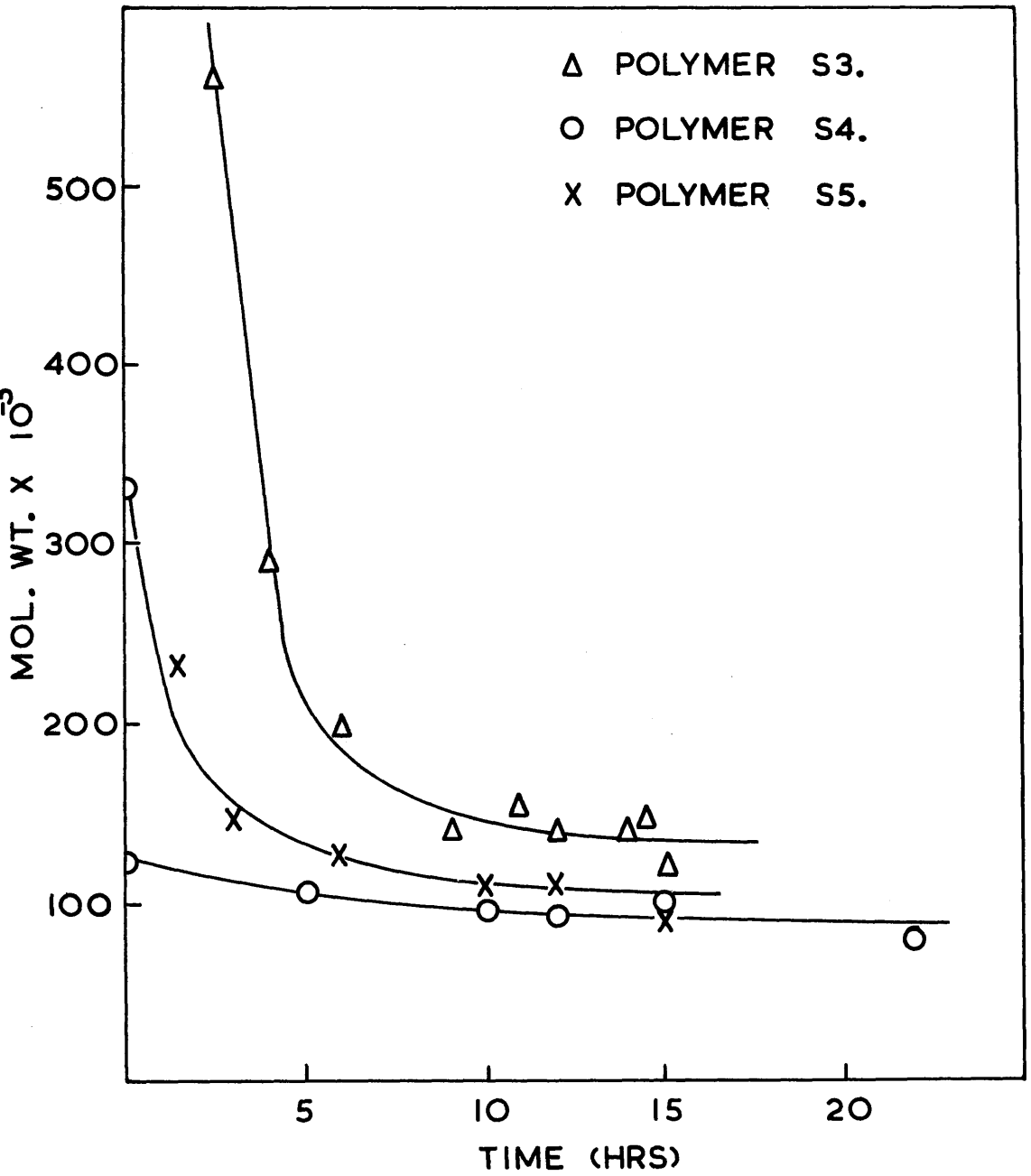

Δ POLYMER S3.
O POLYMER S4.
X POLYMER S5.
500
400
300
200
100
MOL. WT. X 10^{-3}
5
10
15
20
TIME (HRS)

FIG. 24.

(iv) Molecular Weight of The Undegraded Polymer -

When molecular weight is plotted against time during the ultrasonic or mechanical degradation of polystyrene it is found that, irrespective of the molecular weight of the undegraded material, degradation appears to come to a standstill at a molecular weight of approximately 100,000.[54,55] The extent of chain scission during this reaction is clearly dependent on the molecular weight of the undegraded material.

The molecular weight-time curves for polymers S.3, 4 and 5, at 290°C, are shown in Fig. 24 and it can be seen that here again the molecular weight falls to a limiting value which does not differ greatly from that reported for mechanical and ultrasonic degradation. This raises the possibility that the thermal degradation of polystyrene is also governed by molecular weight rather than by the presence of weak links distributed at random along the polymer chain. Attention has already been drawn (see page 75) to the possible similarity of both degradative processes.

The close agreement between the values of S recorded for polymers S.3 and S.6 would suggest, however, that degradation does not depend on the chain length of the molecule. The molecular weight-conversion curves for S.3 and S.5 provide additional evidence to support this. Since

chain scission can be detected in polymers of molecular weight 130,000 and lower, the values of M_d, 180,000 and 140,000 respectively for polymers S.3 and S.5, cannot be accounted for if chain scission depends on molecular weight. Degradation in these polymers is clearly complete at values below which chain scission would still be expected if this reaction was dependent on the chain length of the molecule.

Although these results are clearly incompatible with the conclusion that S is dependent upon the molecular weight of the undegraded polymer, it must nevertheless be admitted that examination of Table X reveals there is some tendency for S to increase with molecular weight as well as with temperature. This is, however, almost certainly due to an unfortunate choice of polymerisation conditions.

7. Summary

From the results and discussion above it is quite certain that the weak links in polystyrene are in no way associated with chain branches or the method used to initiate polymerisation in the preparation of the polymers.

There is, on the other hand, quite clearly a tendancy for the number of weak links to increase with the temperature of polymerisation. This suggests that weak links are structural abnormalities formed in a process which competes with the polymerisation propagation step. The

most obvious explanation is that this is the head to head addition of monomer units. This does not, however, adequately account for several features of the reaction, in particular values of s less than unity and the lower rate of chain scission of poly-α-deuterostyrene. An alternative abnormal propagation step which does account for these discrepancies is the reaction of the polystyrene radical through the para position of the benzene ring, although it is not immediately clear why this reaction should be favoured by an increase in the temperature of polymerisation.

It is unfortunate that there is a tendency for the molecular weights of the polymers under discussion also to increase with the temperature of polymerisation. This is entirely due to the choice of polymerisation conditions. It does mean, however, that a certain amount of doubt remains as to whether the extent of chain scission may depend upon molecular weight. The balance of evidence is undoubtedly in favour of the temperature effect but in order to establish this beyond doubt it will be necessary to investigate several more polymers and in particular some very high molecular weight samples prepared in the lower temperature ranges.

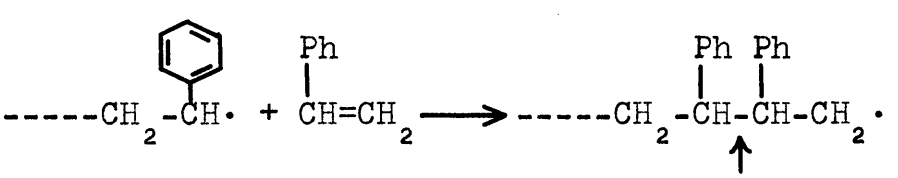
CHAPTER V

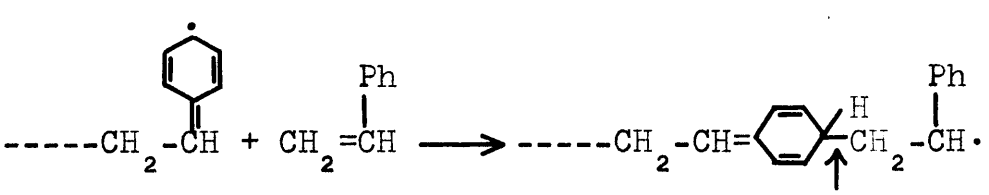
THE DEGRADATION OF ISOTACTIC AND IONIC POLYSTYRENE

I. THE DEGRADATION OF IONICALLY POLYMERISED POLYSTYRENE

1. Introduction

Discussion so far has been limited to the degradation of polymers prepared by a free radical process, and it has been suggested that this is governed by chain scission at a limited number of weak links present in the polymer chain which are produced by the abnormal addition of monomer units to the free radical end of the growing polymer chain -





A potentially weak carbon-carbon bond, indicated by the arrows in the above formulae, may be produced by either of these reactions.

Styrene may, however, be polymerised ionically and this offers the opportunity of examining the degradation characteristics of a polymer in which addition of the monomer units during polymerisation is governed by the presence of iono. These may exert a polarising influence on the monomer and so determine the mode or direction of addition.

It was therefore decided to examine the degradation of ionically polymerised polystyrene and the system selected for the preparation of the polymer was styrene - stannic chloride in ethyl chloride.

2. Preparation of the Polymer.

The cationic polymerisation of styrene is comparatively free from many of the complicating side reactions which characterise the ionic polymerisation of other olefins, and polymers up to a molecular weight of approximately 40,000 can be obtained at room temperature by suitable choice of both catalyst and solvent.[58] For direct comparison with the thermal polymers already examined it was, however, desirable to obtain a polymer whose molecular weight was not less than 100,000. The molecular weight of ionic polymers is known to increase as the temperature of polymerisation is lowered, and it was found in the present instance that a polymer of suitable molecular weight could

be obtained by carrying out the polymerisation at -72°C.

The solvent and catalyst employed in the polymerisation were ethyl chloride and stannic chloride respectively (B.D.H. Ltd.). These were not further purified. The monomer (Mersey Chemicals Ltd.) was dried over calcium chloride and distilled under reduced pressure before use, as in all previous polymerisations.

The reaction was carried out in a beaker immersed in a freezing mixture of solid carbon dioxide and methanol, -72°C. The solvent (150 ml) and monomer (45 ml) were cooled in the reaction vessel for forty-five minutes before the catalyst was added, to ensure that the system was at the temperature of the freezing mixture. The catalyst (5 ml) was then added dropwise from a burette into the solvent-monomer mixture which was kept thoroughly stirred throughout the course of the reaction. After about an hour the polymer was isolated by pouring the reaction mixture into methanol. The polymer was then reprecipitated and dried using the same procedure as that employed for the thermal polymers previously described. In this way about 2.26 gms., corresponding to approximately 5% polymerisation, of a polymer of molecular weight 129,600 were obtained.

3. Results

The results for the degradation of this polymer at 290°C are given in Table XI and the molecular weight-

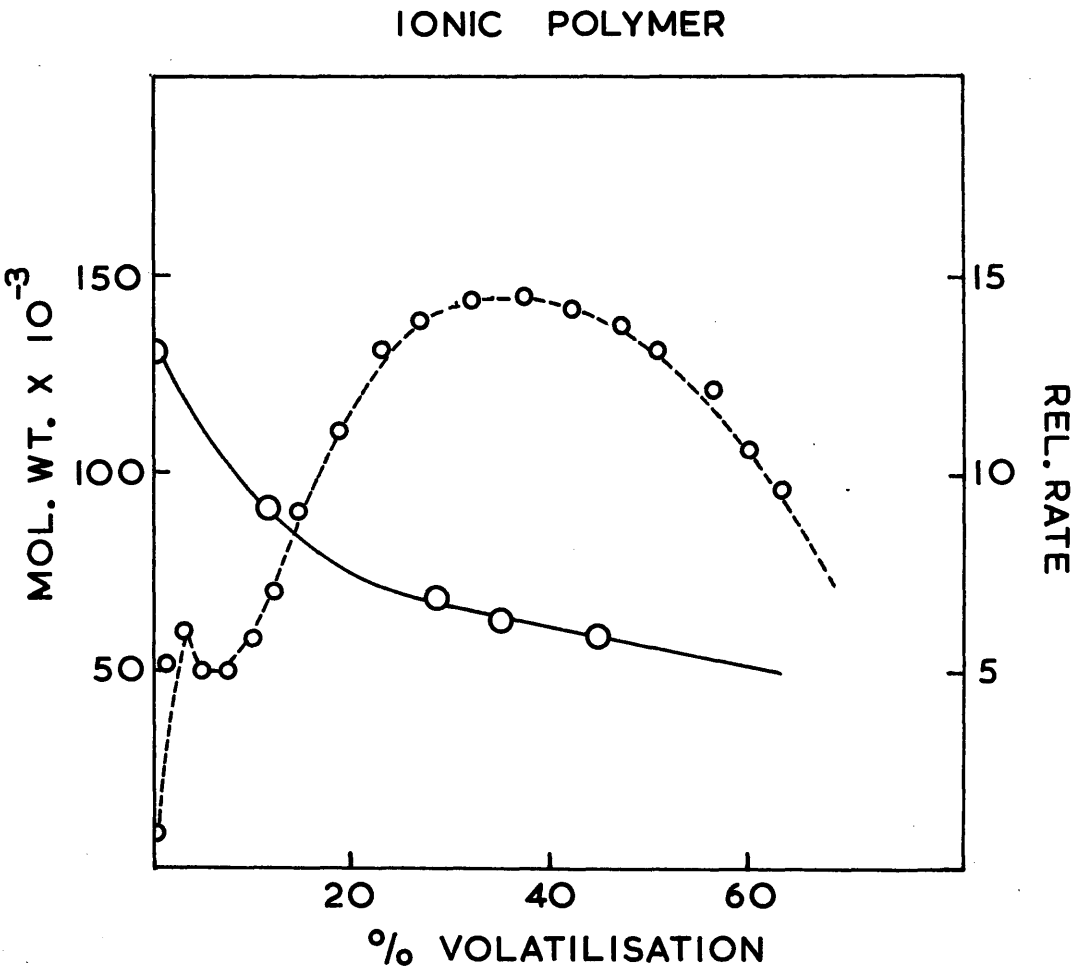

IONIC POLYMER
MOL. WT. X 10^{-3}
150
100
50
REL. RATE
15
10
5
20
40
60
% VOLATILISATION

FIG. 25.

conversion curve is shown in Fig. 25.

TABLE XI

Degradation of Ionic Polymer

Molecular Weight - 129,600

Temp. °C	Time (Hrs.)	Mol. Wt.	% Volatilisation
290	10.0	90,220	11.80
290	20.0	67,920	28.42
290	25.0	62,530	34.97
290	30.0	58,480	45.19

Also shown in Fig. 25 is the relationship between the rate of volatilisation and percentage conversion to volatile material, determined by degrading the polymer at 320°C.

The extrapolation of the curve of molecular weight versus percentage volatilisation to zero extent of degradation, obtained by drawing the best line through the three points available, gives M_d as 80,000. The number of bonds broken per molecule, s, and per monomer unit, S, can then be calculated with the following result:-

M_o	M_d	s	S
129,600	80,000	0.62	4.95×10^{-4}

Even allowing for the maximum possible error in the extrapolation, S must be in the range 4.2 to 5.8×10^{-4}.

4. Discussion

Reference to Fig. 25 shows that the principle features of the degradation of polystyrene have remained unaltered as a result of the change in the mechanism of polymerisation. The molecular weight still falls off rapidly up to 30% volatilisation and the maximum rate of volatile production again approximates to the point of inflexion of the molecular weight-conversion curve. Degradation must therefore still proceed through chain scission at weak links distributed at random along the polymer chain.

It is interesting to compare the results obtained for the ionic polymer with those obtained for polymer S.11, which is of approximately the same molecular weight -

Polymer	M_o	M_d	s	S
Ionic	129,600	80,000	0.62	4.95×10^{-4}
S.11	130,200	100,000	0.30	2.41×10^{-4}

It can be seen that the number of bonds broken per molecule on the ionic polymer is approximately double the number broken in the polymer prepared by a free radical

mechanism. While it might be suggested that this provides further evidence that the molecular weight of the polymer does not influence the degradation, differences in the distributions of the ionic and thermal polymers may render this conclusion subject to some qualification, although it is extremely doubtful whether this factor could account for a difference in the values of s of the order of magnitude observed. Further comparison of the values of s for the ionic and thermal polymers cannot, however, be made in view of the different mechanisms of polymerisation.

It has already been shown in the case of thermal polymers that the nature of the chain ends does not affect the chain scission phase of the reaction. It is therefore also unlikely that the chain ends produced by the initiation and termination reactions in the ionic polymerisation of styrene will in any way influence the degradation of the polymer. Attention must therefore again be focussed on the propagation reaction as the most probable source of weak link formation.

Although the mechanism of ionic polymerisation is as yet incompletely understood, it is generally acknowledged that the presence of impurities, such as water, in the polymerisation medium would appear to be necessary for the formation of the initiation complex. These

impurities have therefore been termed cocatalysts. In the system styrene-stannic chloride in ethyl chloride, the presence of cocatalysts such as water, or hydrogen chloride formed by the hydrolysis of the catalyst, does not appear to be necessary. The cocatalyst in this system may, however, be provided by the solvent itself.[58]

It has been suggested that these cocatalysts, here generalised in the formula AB, react in the following way -

$$S_nCl_4 + AB \longrightarrow S_nCl_4.AB \rightleftharpoons S_nCl_4.B^{\ominus} + A^{\oplus}$$

and that polymerisation is initiated by the formation of the carbonium ion -

$$S_nCl_4.AB + CH_2{=}\overset{\overset{Ph}{|}}{CH} \longrightarrow A.CH_2\text{-}\overset{\overset{Ph}{|}}{CH}^{\oplus} + S_nCl_4.B^{\ominus}$$

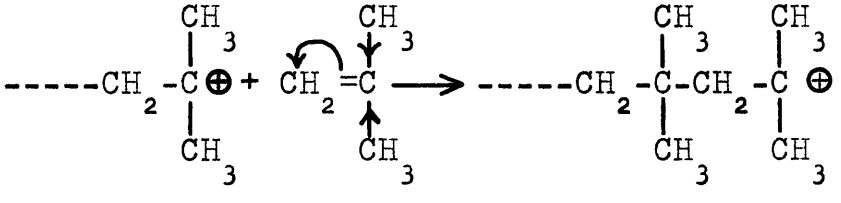
In the system at present under consideration A may be C_2H_5 or H and B, Cl or OH, depending upon whether the cocatalyst is ethyl chloride, hydrogen chloride or water.

Propagation then proceeds through the addition of monomer to the carbonium ion -

$$\text{-----}CH_2\text{-}\overset{\overset{Ph}{|}}{CH}^{\oplus} + S_nCl_4.B^{\ominus} + CH_2{=}\overset{\overset{Ph}{|}}{CH} \longrightarrow$$

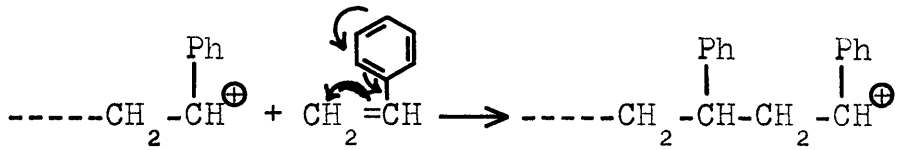
$$\text{-----}CH_2\text{-}\overset{\overset{Ph}{|}}{CH}\text{-}CH_2\text{-}\overset{\overset{Ph}{|}}{CH}^{\oplus} + S_nCl_4B^{\ominus}$$

Head to tail addition of monomer units is again preferred, as in free radical polymerisation. This is due to the fact that the transition state for the addition of monomer in an ionic polymerisation is such that the incoming molecule is highly polarised. The orientation favoured for monomer addition will therefore be that which permits maximum polarisability, and as this is determined by the character of the substituents in the monomer, which are generally electropositive, addition through the least substituted end of the double bond would be predicted. Thus for example in the polymerisation of isobutene the inductive effect of the methyl groups would favour addition in the following way -

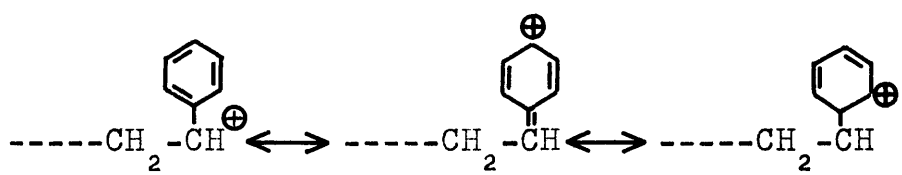


It is much more difficult to interpret the role played by the benzene ring in the ionic polymerisation of styrene, since it is known to be capable of acting both as an electron source and as an electron sink.

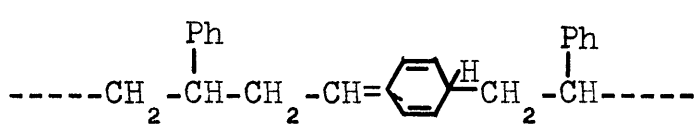
Under the influence of an electrophilic reagent such as the carbonium ion, the phenyl group in the styrene molecule would be expected to act as an electron source[59] -



thus favouring the head to tail addition of monomer units. Polarisation of the olefinic double bond in the opposite sense to that indicated above may, however, also be possible due to the ability of the benzene ring to act as an electron sink, and this would offer the opportunity for the head to head addition of monomer units. Head to tail addition would, nevertheless, still be favoured from energy considerations as in free radical polymerisation, because of the possible resonance stabilisation by the benzene ring of the electron difficient carbonium ion -



The existence of these resonance structures will also render possible the propagation of the polymer chain through the para position of the benzene neucleus and the formation of structures of the type -



may also occur.

5. Summary

The rapid fall in molecular weight during the initial stages of the degradation of the ionic polymer can reasonably be explained in terms of the same structures which are probably responsible for weak link scission in thermal polymers.

While the head to tail addition of monomer units would appear to be favoured not only from energy considerations but also by the polarising influence of the carbonium ion on the styrene molecule, the possible contribution of this last effect towards the exclusion of head to head addition is somewhat doubtful because of the apparent ability of the benzene ring in styrene to act both as an electron source and acceptor.

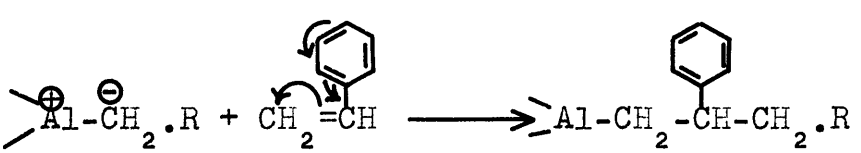
II. THE DEGRADATION OF ISOTACTIC POLYSTYRENE

Within the last two years considerable interest has been aroused by the synthesis of a new class of high polymers by NATTA and his co-workers in Italy.[60] These polymers, termed isotactic, are prepared by an ionic mechanism using heterogeneous catalysts of the type $Al.Et_3/TiCl_4$, and differ from polymers normally produced in either free radical or ionic polymerisations in many of their physical properties. In particular they exhibit a very

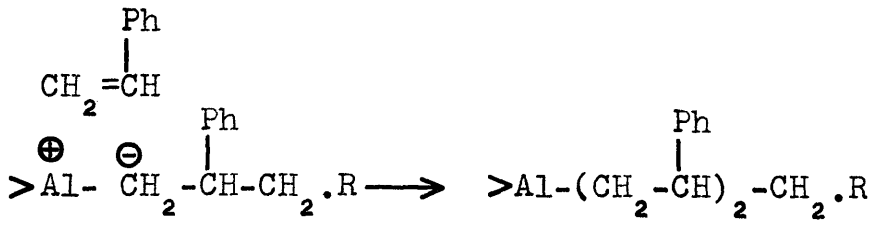
high degree of crystallinity, a property unusual in high polymers. Natta has pointed out that the amorphous character of high polymers of the type, $(CH_2\text{-}CHX\text{-})_n$ is, in general, usually attributed to configurational variations in the disposition of the atoms or groups on the asymmetric carbon atoms along the chain and also to some extent to the occurence of chain branching. He has therefore suggested that the crystalline nature of these new polymers must be associated with the stereospecific orientation of the monomer units in the polymer chain.

Although little is yet known of the mechanism of polymerisation, evidence has been reported for the presence in the isotactic polymer of the alkyl group present in the aluminium alkyl of the catalyst, and this, together with infra-red evidence for the presence of a terminal double bond, has led to the suggestion that polymerisation takes place by the insertion of monomer between the metal of the catalyst and the pendant alkyl group [61] -

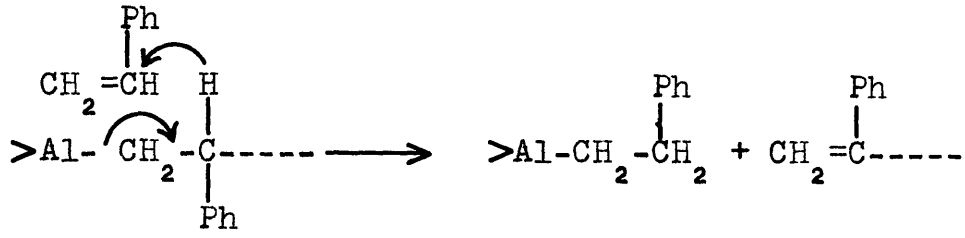
Initiation probably occurs as follows -



propagation following the same course -



The existence of the terminal double bond might be explained in terms of the reaction -



The stereospecific mode of addition probably arises by virtue of the absorbed nature of the growing chain end and the proximity of the catalyst surface which will reduce the rotational freedom of the monomer during addition. It has also been claimed that polymerisation takes place by the vigorous head to tail addition of monomer units.

NATTA, PINO and MAZZANTI[62] have followed the change in molecular weight during the degradation of isotactic polystyrene from measurements of the intrinsic viscosity of the polymer as it degraded. The curve obtained by these authors for the degradation of an ionic polymer in boiling tetralin (206°C), under an atmosphere of nitrogen is shown

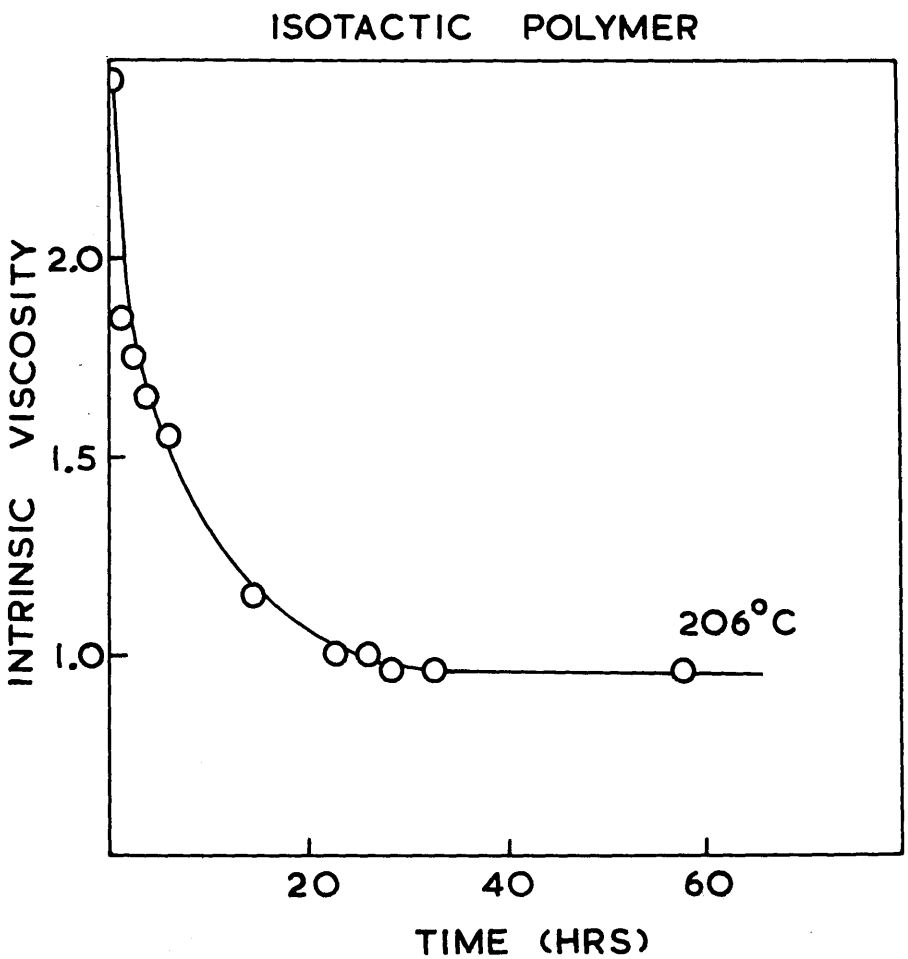

ISOTACTIC POLYMER
INTRINSIC VISCOSITY
2.0
1.5
1.0
206°C
20
40
60
TIME (HRS)

FIG. 26.

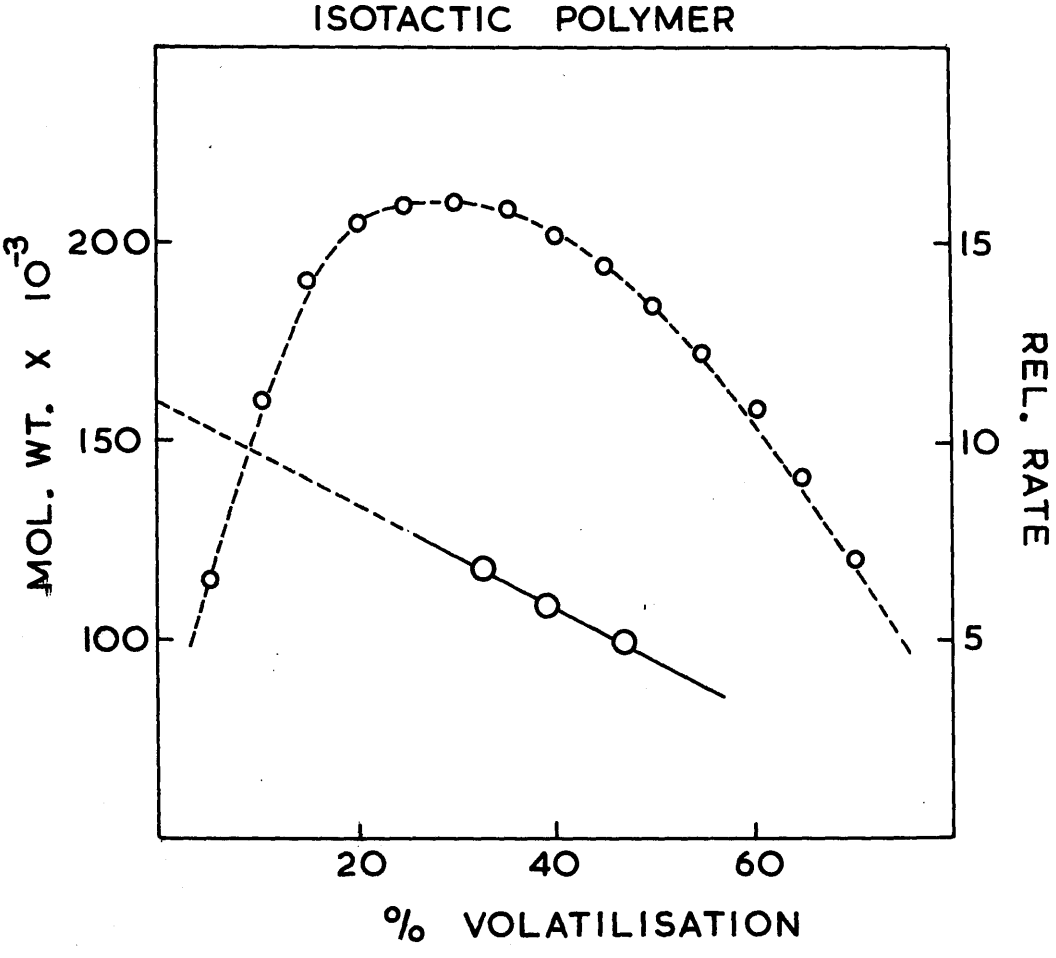

ISOTACTIC POLYMER
MOL. WT. X 10^{-3}
200
150
100
15
10
5
REL. RATE
20
40
60
% VOLATILISATION

FIG. 27.

in Fig. 26. This does not differ in any respect from the type of curve previously obtained for either thermal (i.e. polymers prepared by a free radical process) or ionic polymers, and would again suggest that the mechanism of degradation is exactly similar to that occurring in these systems. Further confirmation of this was obtained during the present investigation by degrading a commercial sample of isotactic polystyrene, prepared by the method given in a patent granted to Montecatini[63], at 320°C and following the rate of volatile production as the reaction proceeded. The conversion-rate curve is shown in Fig. 27. It can be seen that this exhibits the same features as the corresponding curve for thermal and ionic polymers.

It was unfortunately impossible, due to the insolubility of the undegraded polymer in benzene at room temperature to completely evaluate the molecular weight-conversion curve. It was, however, found that approximately 90% of the polymer residue could be dissolved in benzene after the polymer had been degraded at 290°C to 30% conversion, and the results for this and successive degradations to 40 and 50% volatilisation are given in Table XII and Fig. 27.

TABLE XII

Degradation of Isotactic Polymer

Molecular Weight - Unknown

Temp. °C	Time	Mol. Wt.	% Volatilisation
290	14.0	115,900	33.08
290	16.0	106,600	39.72
290	18.0	97,050	47.32

From these it would appear that the molecular weight-conversion curve beyond 30% conversion is again linear, as in all previous cases, and the molecular weight to which the polymer degrades, 160,000, also falls into the range noted for values of M_d for thermal polymers.

It must therefore be concluded that the formation of weak links is still possible despite the apparent stereospecific nature of the polymerisation process. It would, however, be unwise, both in view of the limited amount of experimental data at present available and the probable complex nature of the transition state for monomer addition, to attempt to discuss further the mechanism by which these could be formed.

CHAPTER VI.

THE PROBLEM REVIEWED

It is not intended here to summarise in detail the results of the present investigation. This has already been done in the conclusions to the foregoing chapters. Instead a broad general survey of the work just described will be given and attention will be drawn to further possible courses of investigation.

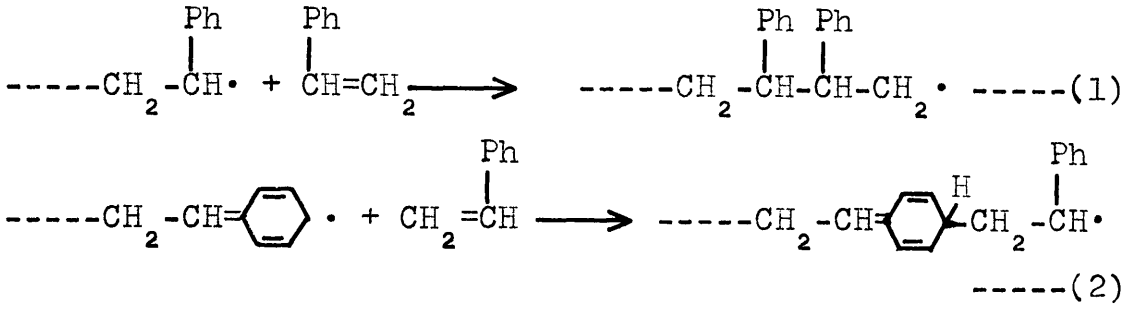
The results of the present investigation have clearly established that the thermal degradation of polystyrene is associated with the presence of weak links in the polymer chain. It has been shown that two separate processes occur during the degradation. In the initial stages of degradation the predominant reaction is that of chain scission, superimposed on which is a reverse polymerisation reaction from the chain ends. Weak link scission is complete by the time 30% of the polymer has been volatilised in this latter reaction, and beyond this conversion degradation takes place exclusively be depropagation from the chain ends. The chain length

of the reverse polymerisation reaction is estimated to be of the order of 600.

It has also been suggested that the increase in the rate of production of volatile material observed during the reaction, can best be explained by assuming that chain scission takes place by disproportionation in a reaction akin to that occurring in the termination step in polymerising systems. The production of volatile material can then be regarded as following the subsequent breakdown of the chain ends produced, and in this way the increasing rate of volatile production can be associated with the increasing number of degradable chain ends formed during the chain scission process.

Regarding the nature of the weak links themselves it has been shown that the presence of oxygenated structures in the polymer chain is not primarily responsible for the formation of weak links. The nature of the chain ends and the occurrence of chain branching have also been eliminated as possible sources of weak links. Although the exact chemical structure of the weak link has not been determined the increasing number of weak links present as the temperature of polymerisation is raised, has been interpreted as indicating that weak links are formed in a reaction which competes with the normal propagation step in the polymerisation process. Two such reactions which

may be responsible for weak link formation have been formulated -



Of these, reaction (2) offers the best explanation of the experimental results. On the basis of this structure it is possible to explain the fact that poly-α-deuterostyrene degrades more slowly than polystyrene itself, since chain scission by disproportionation must involve the transfer of the α-hydrogen atom. It is also possible to explain, if this weak link structure is assumed, values less than unity observed for the number of bonds broken per molecule in polymers of low molecular weight. Previous discussion (see pages 83 to 88) has shown that neither of these facts can be explained on the basis of the weak link structure formed in reaction (1). It must, nevertheless, be admitted that it is not exactly clear why reaction (2) should be more favoured as the temperature of polymerisation is raised.

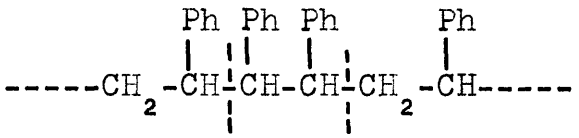
Finally attention must be drawn to the results outlined in Chapter V, which show that the formation of weak links also occurs in both ionic and isotactic

polymerisations. These may, however, also be explained in terms of ionic variants of reactions (1) and (2).

It has already been pointed out during discussion of the results in Table X (Page 81) that there would appear to be a tendency for the number of weak links present to increase with molecular weight as well as with temperature of polymerisation. While more detailed consideration of the results shows that the bulk of experimental evidence does not support this view it would, nevertheless, be advisable to confirm this by examining the degradation of a high molecular weight polymer prepared at 30°C: On the assumption that this confirmed the previous findings attention could then be devoted to the final problem - that of determining the weak link structure.

It might be suggested that the copolymerisation of 2:3-diphenyl butadiene with styrene might afford the opportunity of investigating whether the head to head addition of monomer units was responsible for weak link formation. This would, however, present many new structural problems such as the possible presence in the polymer chain of structures arising out of 1:2- addition, and the elimination of the double bond which would remain in the polymer chain as a result of the normal mode of 1:4- addition.

The copolymerisation of stilbene with styrene presents a much simpler system for study, and although this does not strictly reproduce the same structure as the head to head addition of monomer units,



comparison of the degradation characteristics of a polymer which contained a small amount of stilbene with those of a polymer free from this monomer might provide some useful information regarding the structure of the weak link.

The presence of structures produced in reaction (2) above would be much more difficult to diagnose but if ozonolysis of the polymer followed by a re-examination of the molecular weight revealed the presence of double bonds in the polymer chain, these would be difficult to account for in terms of a reaction other than that already formulated. A careful examination of the infra-red spectrum of the polymer might also prove extremely useful at this point in the investigation.

The difficulty of analysing the molecular weight-conversion curves in terms of the chain scission and depropagation reactions has already been mentioned and the accompanying difficulty of determining the value of the molecular weight to which the polymer degrades as a result

of the chain scission reaction alone, has also been discussed. Both of these difficulties could be eliminated if a suitable inhibitor for the reverse polymerisation reaction could be found which is stable at the elevated temperatures of degradation. This would also resolve in a completely unambiguous manner the nature of the chain scission process as a clear distinction could then be drawn between weak link scission and intermolecular transfer. This would be apparent from the nature of the molecular weight - time curves alone.

In conclusion then it can be claimed that the nature of the degradation of polystyrene has been resolved and that an explanation of the various features of the degradation, previously reported by other workers, has been provided within the limits of the Weak Link Theory. It has also been clearly established for the first time that weak links are formed during the polymerisation process itself and that oxygenated structures are not primarily responsible for their formation. Although the exact nature of the weak link has not been defined it would appear more than probable that these are formed during the propagation step in polymerisation and two reactions which might explain their formation have been formulated.

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